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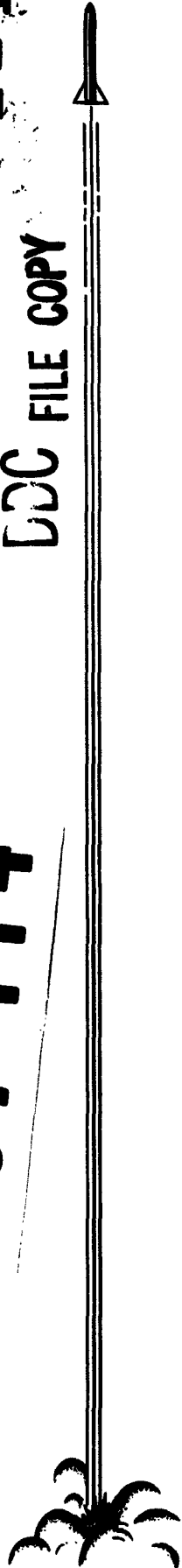
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Report RMD-AOR-Q1-63

(U)

ADVANCED OXIDIZER RESEARCH

COMBINED REPORT
Projects 076, 5007, 5017 and 5009

30 April 1963

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Thiokol ®

CHEMICAL CORPORATION

REACTION MOTORS DIVISION
DENVILLE. NEW JERSEY

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ADVANCED OXIDIZER RESEARCH

30 April 1963

Report RMD-AOR-Q1-63

Contract No.	ARPA Order No.
Contract No. NOnr 1878(00),	ARPA Order No. 186-61
Contract No. NOnr 3664(00),	ARPA Order No. 23-62
Contract No. NOnr 3913(00),	ARPA Order No. 354-62
Contract No. NOnr 3824(00),	ARPA Order No. 314-62

Submitted by:
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Director of Research

ARPA Cont. No. 1668

This report has been distributed in accordance
with a combined LPIA-SPIA Distribution List in
effect as of the publication date of this report.

GENERAL FOREWORD

This quarterly report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry being conducted at this Division under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, and was conducted under the following contracts:

RMD Project No.	Contract No.	ARPA Order No.	Title
076	NOnr 1878(00)	186-61	Difluoramine Chemistry
5007	NOnr 3664(00)	23-62	Structure-Sensitivity Study
5017	NOnr 3913(00)	354-62	Stabilization of High Energy Solid Oxidizer
5009	NOnr 3824(00)	314-62	Inorganic Chemistry of the Oxygen Subfluorides

Reports on these programs were previously issued separately. Since the reporting dates did not coincide in all cases, the time periods covered for the separate programs are not exactly the same. The actual time period covered on each task is indicated in the Foreword to the appropriate section of the report. Future reports will also be issued on a calendar quarter basis on all these programs.

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GENERAL INTRODUCTION

This report describes research conducted at Thiokol Chemical Corporation, Reaction Motors Division directed toward the development of advanced solid oxidizers. The four major tasks on which work has been performed are listed below, together with the objective of each task, and are included as four separate sections of this report.

SECTION I. RMD PROJECT 076 - DIFLUORAMINE CHEMISTRY

Investigation of the chemical reactions of the organic difluoramines.

SECTION II. RMD PROJECT 5007 - STRUCTURE-SENSITIVITY STUDY

Preparation of a series of organic difluoramines for evaluation of the relationship between structure and sensitivity.

SECTION III. RMD PROJECT 5017 - STABILIZATION OF HIGH ENERGY SOLID OXIDIZER

Investigation of the reactions of NO_2ClO_4 with various ligand molecules in an effort to increase the size of the NO_2^+ cation and thereby improve the stability of NO_2ClO_4.

SECTION IV. RMD PROJECT 5009 - INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

Investigation of the chemical reactions of O_2F_2 and other oxygen subfluorides in an effort to discover new reactions leading to solid oxidizers containing oxygen and fluorine.

Section I

RMD Project 076

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DIFLUORAMINE CHEMISTRY

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Section I

(U)
DIFLUORAMINE CHEMISTRY

H. F. Smith

Report RMD-AOR-Q1-63

RMD Project 076
Report Period: 1 January 1963 to
                31 March 1963

Contract No. NOnr 1878(00)
ARPA Order No. 186-61
Project Code No. 3910

This report has been distributed in accordance
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effect as of the publication date of this report.

FOREWORD

    This section of the quarterly report covers research conducted during the period from 1 January 1963 to 31 March 1963 on the chemical reactivity of alkyldifluoramines (RMD Project 076).

    Technical personnel contributing to this work included: H. F. Smith (Project Scientist), and J. Castellano (Synthesis), and R. Storey, D. Yee, J. Creatura, and A. Fremmer (Instrumental and Wet Chemical Analysis).

CONTENTS

ABSTRACT

An improved synthesis of tert-butyldifluoramine, based upon the thermally initiated reaction between tert-butyl iodide and tetrafluorohydrazine, has been developed. The method consistently gave 40% yields in one step, from a readily available starting material. At higher temperatures, some 1,2-bis(difluoramino)-2-methylpropane was formed, at the expense of the primary product.

Additional evidence has been accumulated supporting the interpretation of the reaction between tert-butyldifluoramine and phenyllithium as a one-electron reduction process involving free radical intermediates. The alkyldifluoramine reacted with n-butyllithium in a similar fashion, to produce n-octane.

Concentrated nitric acid was reduced by tert-butyldifluoramine to nitrogen tetroxide. Carbon dioxide and mixed alkyl nitrites were also formed.

I. INTRODUCTION

The objective of this research program is to investigate the chemical properties of alkyldifluoramines and to elucidate the mechanisms of those reactions which are found to occur. Such information can be applied in the development of useful new synthetic reactions in difluoramine chemistry, as well as in the effective utilization of related nitrogen-fluorine compounds in high energy propellants. In addition, some of the knowledge gained might contribute to the solution of fundamental chemical problems of much broader scope.

A system for the classification of chemical reactivity studies was presented in the Annual Technical Summary Report for 1962 (Ref 1). This system is based upon the nature of the reagents being studied, i.e., atoms or free radicals, electrophilic and nucleophilic reagents, and oxidizing and reducing agents. Our research efforts during the present report period have been directed toward two of these general areas.

The one-electron reduction of tertiary alkyldifluoramines by organometallic compounds (Ref 2) has been explored in greater detail, and additional evidence supporting the proposed mechanism has been accumulated. Reactions of tert-butyldifluoramine with both phenyllithium and n-butyllithium have been studied.

An investigation of the reaction of tert-butyldifluoramine with concentrated nitric acid was initiated during the present quarter. Although the identification of products and the delineation of the stoichiometry and mechanism of the reaction have not yet been completed, a discussion of the significance of preliminary observations is included in this report.

A new, convenient, and more efficient synthesis of the model compound, tert-butyldifluoramine, has been developed, and details of the procedure are described.

II. DISCUSSION

A. PREPARATION OF TERT-BUTYLDIFLUORAMINE

When tert-butyldifluoramine (II) was first adopted as a model compound for these studies (Ref 3), the only known method of synthesis involved the photolysis of a mixture of tetrafluorohydrazine and azoisobutane (Ref 4) (equation 1). The yield of purified product was only 20% of theory (Ref 2).

$$N_2F_4 + (CH_3)_3CN=NC(CH_3)_3 \longrightarrow 2(CH_3)_3CNF_2 \qquad (1)$$

$$\text{I} \qquad\qquad\qquad \text{II}$$
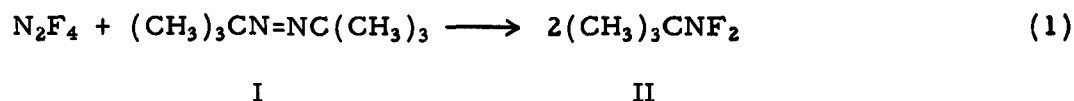
In addition, the synthesis of I (Ref 5, 6) proceeded with a yield of only 30%, giving a 6% overall yield for the two-step process.

Since the use of substantial quantities of II was anticipated, a more efficient method of synthesis was sought. The direct fluorination of the isomeric n-butylamine in aqueous medium (equation 2) had been reported (Ref 7).

$$C_4H_9NH_2 + 2F_2 + 2NaHCO_3 \xrightarrow{\;H_2O\;} C_4H_9NF_2 + 2NaF + 2H_2O + 2CO_2 \qquad (2)$$

Attempts to apply this method to the preparation of the tert-butyl analog, however, were unsuccessful (Ref 1).

Other simple alkyldifluoramines have been produced by the photolysis of the corresponding alkyl iodides in the presence of tetrafluorohydrazine (Ref 8). This method has now been applied to the synthesis of tert-butyldifluoramine (equations 3, 4, 5 and 6).

$$(CH_3)_3CI \longrightarrow (CH_3)_3C\cdot + I\cdot \qquad (3)$$

$$N_2F_4 \rightleftharpoons 2\,\dot{N}F_2 \qquad (4)$$

$$(CH_3)_3C\cdot + \cdot NF_2 \longrightarrow (CH_3)_3CNF_2 \qquad (5)$$

$$\text{II}$$

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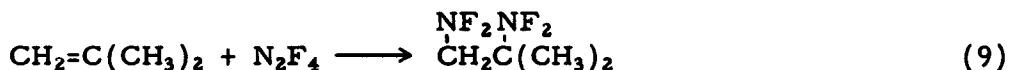$$2 \; I\cdot \; \rightleftharpoons \; I_2 \tag{6}$$

Furthermore, experiment has shown that the same results obtained by photolysis can be achieved by thermal activation, with a consequent decrease in reaction time from 20 hours to 3-4 hours. Yields of 40% of the desired model compound have been obtained routinely using this technique. No increase in yield was observed when the reaction time was increased to six hours. The distilled product was identified by comparison of its boiling point and infrared and mass spectra with those of a sample prepared by the azoisobutane method.

The identification of the by-products of the reaction is of interest as a possible means of effecting still further improvement in the yield. A mixture of the gaseous products was examined by infrared and mass spectrometry, and found to contain N_2, NO, N_2O_4, N_2F_4, CF_4, C_2F_6, and SiF_4. The fluorocarbons are known contaminants in the tetrafluorohydrazine used. The nonvolatile tarry residue consisted principally of iodine and polymeric material. No evidence for the formation of 2,2,3,3-tetramethylbutane, from the coupling of two tert-butyl radicals, was found (equation 7).

$$2(CH_3)_3C\cdot \; \xrightarrow{\;\;\diagdown\;\;} \; (CH_3)_3C\text{-}C(CH_3)_3 \tag{7}$$
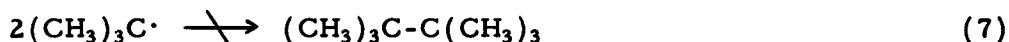
In one instance, in which the reaction temperature was 110°C instead of the usual 80-100°C, the yield of tert-butyldifluoramine decreased to 25%. In addition, there was obtained in 24% yield a liquid (bp 115°C) which was identified by its infrared spectrum as 1,2-bis(difluoramino)-2-methylpropane (III). The infrared spectrum of this compound is reproduced in Figure 1. This observation may be explained by the mechanism outlined in equations 8 and 9.

$$2(CH_3)_3C\cdot \; \longrightarrow \; (CH_3)_3CH \; + \; CH_2\text{=}C(CH_3)_2 \tag{8}$$

$$CH_2\text{=}C(CH_3)_2 \; + \; N_2F_4 \; \longrightarrow \; \overset{NF_2 \; NF_2}{\underset{|\;\;\;\;|}{CH_2C(CH_3)_2}} \tag{9}$$

III

Either thermodynamic or kinetic considerations, or a combination of both, may be involved in this side reaction. It may be that an increase in temperature accelerates the reaction shown in equation 8 to a greater extent than that in equation 5. Alternatively, the increase in concentration of tert-butyl free radicals produced by increasing the temperature would be expected to increase the probability of the disproportionation reaction (equation 8). This explanation assumes that the increase in concentration of NF_2 radicals with increasing

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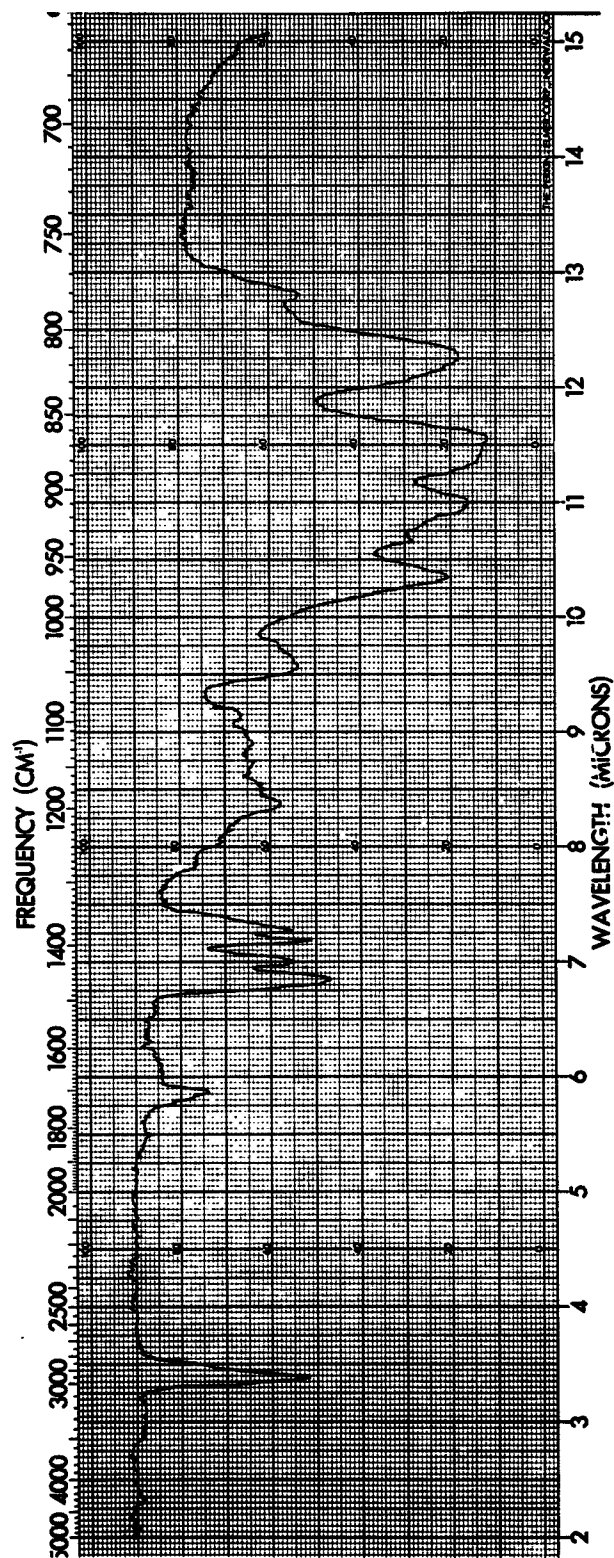

Figure 1. Infrared Spectrum of 1,2-bis(Difluoramino)-2-methylpropane

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temperature is not proportionately great. In either case, the addition step (equation 9) must be reasonably rapid.

B. REACTIONS OF TERT-BUTYLDIFLUORAMINE WITH ORGANOMETALLIC COMPOUNDS

A preliminary investigation of the reaction of tert-butyldifluoramine with phenyllithium has been described in previous reports (Ref 1, 2). This reaction has now been repeated essentially as before, but on a larger scale (23 mmoles) to permit more complete recovery of products. In this instance, the organic portion of the reaction mixture was fractionated by distillation through a Vigreaux column. The first six fractions, collected at atmospheric pressure, consisted of mixtures of ether and benzene containing traces of starting material and biphenyl. The seventh fraction, weighing 0.25 g, boiled at 95-110°C at 0.1 mm. This fraction was found to be a complex mixture, showing infrared absorptions indicative of O-H, C=O, N-F, C-O-C, and substituted aromatic groupings. Attempts to separate this mixture into its constituents by gas chromatography are in progress.

The eighth distillation fraction, weighing 0.85 g, was mainly biphenyl. This is more than twice the amount of biphenyl contained in a corresponding sample of the phenyllithium reagent. It is clear then that a significant amount of biphenyl was formed in the reaction, and this fact lends further weight to the one-electron reduction mechanism proposed earlier.

The distillation residue, 0.70 g, consisted of mixed aliphatic compounds along with some biphenyl. Gas chromatographic methods will be utilized in an effort to isolate additional products from this fraction.

Analyses of the aqueous extract of the reaction mixture have not been entirely satisfactory. A blank (equal aliquot of the phenyllithium reagent, hydrolyzed with water) was found to contain 19.81 meq of Li^+ and 20.45 meq of OH^-. Comparison of these figures with the theoretical 23.00 mmoles indicates that the reagent is 12.5% lower in concentration than the nominal value. The aqueous solution from the reaction contained 17.67 meq of Li^+, indicating a recovery of 89%. The sum of F^- (5.10 meq) and OH^- (8.60) did not agree with the amount of Li^+ found. The reason for this discrepancy has not yet been determined.

In the same fashion, tert-butyldifluoramine was treated with n-butyllithium in hexane solution. The reaction observed was qualitatively similar to that which occurred when phenyllithium was used. Dark brown products formed

with the evolution of heat. After the reaction was quenched with water, the hexane layer was found to contain some unreacted tert-butyldifluoramine and some n-octane. No products derived from the difluoramine could be detected in the organic portion. The aqueous fraction will be examined for possible water-soluble products and analyzed for the usual lithium, fluoride, and hydroxide.

The production of n-octane suggests that the same reaction path is followed as in the case of phenyllithium. The absence of high-boiling hydrocarbon-soluble products, however, remains to be explained.

C. REACTION OF TERT-BUTYLDIFLUORAMINE WITH NITRIC ACID

Past experience has shown that alkyldifluoramines are oxidized by permangamate, but not by mercuric oxide or neutral hydrogen peroxide (Ref 1, 9). Electrophilic attack by strong acid led to the elimination of hydrogen fluoride from a secondary alkyldifluoramine and difluoramine from a tertiary compound (Ref 1, 10). It is of interest then to determine what type of reaction, if any, occurs between a tertiary alkyldifluoramine and nitric acid.

An investigation into this area has been started. When tert-butyldifluoramine was mixed with concentrated nitric acid, there were no visible indications that reaction had occurred after a few hours at 28 or at 50°C. After standing at room temperature for 16-20 hours, however, the mixture rather abruptly became colored and evolved nitrogen tetroxide. Other products included N_2O, NO_2F, CO_2, SiF_4, and unidentified alkyl nitrites and nitrates. Some unreacted tert-butyldifluoramine was also detected, but no other material containing a nitrogen-fluorine bond was present. Molecular oxygen was not found among the products.

In the preliminary experiments which have been performed so far, it has not been possible to quantitatively determine the amounts of various products formed. Provision for this refinement will be made in future experiments. It will be instructive, for example, to determine whether the amount of dinitrogen tetroxide generated can be correlated with the amount of alkyl-difluoramine consumed. It is known (Ref 11) that the thermal decomposition of nitric acid produces nitrogen tetroxide (equation 10), and it is obviously

$$2HNO_3 \longrightarrow N_2O_4 + H_2O + O \cdot \atop \overset{\downarrow\uparrow}{2NO_2} \tag{10}$$
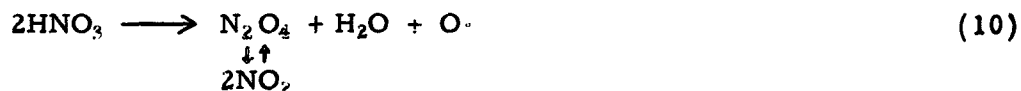
possible that catalytic effects might lower the activation energy so that the reaction might become significant at room temperature. The absence of oxygen in the reaction products tends to argue against this process, but it is also possible that the atomic oxygen formed would react preferentially with the alkyldifluoramine. Quantitative determination of the nitrogen tetroxide formed should help answer these questions.

The appearance of carbon dioxide among the products indicates extensive oxidative degradation of the tert-butyl moiety. The fact that a mixture of alkyl nitrites is produced, in place of solely tert-butyl nitrite, gives further support to this conclusion.

III. EXPERIMENTAL

A. PREPARATION OF TERT-BUTYLDIFLUORAMINE

A 2000 ml pyrex bulb was charged with 6.0 g (4.0 ml, 0.033 mole) of tert-butyl iodide under a stream of dry nitrogen. The bulb was degassed three times by a freeze-thaw technique (-78 to 25°C), and 4.16 g (0.040 mole) of N_2F_4 was condensed in at liquid nitrogen temperature. The bulb was then heated for four hours at 80-100°C. The gases were passed through traps at -78 and -196°C. The -78°C trap contained the crude tert-butyldifluoramine. This process was repeated four times, and the products of all four runs were combined and distilled to yield 5.8 g (0.053 mole, 40.7%) of tert-butyl-difluoramine, (bp 54-56°C) (vapor pressure 227 mm at 25°C).

B. PREPARATION OF 1,2-BIS(DIFLUORAMINO)-2-METHYLPROPANE

The procedure described for the preparation of tert-butyldifluoramine was duplicated, except that two of the four runs were heated to 110°C. The products of all four runs were combined and distilled to yield 3.5 g (25%) tert-butyldifluoramine, bp 55-56°C, and 2.5 g (24%) 1,2-bis(difluoramino)-2-methylpropane, bp 110-115°C. The infrared spectrum of the latter showed absorptions which confirmed the assigned structure.

The residue from two runs was taken up in CH_2Cl_2 and washed with water, $Na_2S_2O_3$ solution, and again with water. The CH_2Cl_2 solution was dried over Na_2SO_4 and filtered. Removal of the solvent left a brown residue which appeared to be degraded polymeric material, as indicated by infrared analysis.

C. REACTION OF TERT-BUTYLDIFLUORAMINE WITH PHENYLLITHIUM

tert-Butyldifluoramine (2.50 g, 0.023 mole) was dissolved in 20 ml of sodium-dried ether, and the solution was cooled to 0°C. Under a stream of nitrogen, 11.5 ml (0.023 mole) of phenyllithium solution in benzene-ether (Lithium Corp. of America), diluted with an additional 10 ml of sodium-dried ether, was added dropwise to the stirred solution at such a rate as to maintain the temperature at 0-5°C. This required about 30 minutes. The dark brown mixture was stirred for one hour at 0°C and then quenched with 20 ml of cold H_2O. The aqueous and organic phases were separated. The aqueous phase

was washed with two 20 ml portions of ether, and the organic phase was washed with two 20 ml portions_of water._ The combined aqueous solution was submitted for analysis for Li^+, F^-, and OH^-. The combined organic extracts were dried over Na_2SO_4 and distilled through a Vigreaux column. The ether and benzene collected were found to contain traces of biphenyl. A liquid, bp 95-110°C/0.1 mm and weighing 0.25 g, was found to be a mixture of materials showing infrared absorption due to C=O, OH (alcohol), N-F, substituted aromatics and C-O-C. This material is being subjected to gas chromatographic separation and mass spectral analysis. In addition, 0.85 g of biphenyl was obtained and a residue weighing 0.70 g remained. This residue appeared to contain biphenyl and other substituted aromatics.

D. REACTION OF TERT-BUTYLDIFLUORAMINE WITH N-BUTYLLITHIUM

tert-Butyldifluoramine (2.20 g, 0.020 mole) was dissolved in 10 ml of hexane and the solution cooled to 0°C. Under a stream of nitrogen, 12.9 ml (0.020 mole) of n-butyllithium in hexane (Foote Mineral Corp.), diluted with 10 ml of hexane, was added dropwise to the stirred solution over a period of one hour. The color of the mixture darkened as stirring was continued for 1-1/2 hours at 20°C. The mixture was then treated with 20 ml of H_2O; no temperature rise was noted. The aqueous and organic phases were separated and treated as above (Section III C), using hexane as the solvent for extraction. The hexane solution was dried over $NaSO_4$ and distilled. The initial distillate, bp 33-68°C, was a mixture of hexane and tert-butyldifluoramine. After removal of the low-boiling fraction, a 1.0 g residue remained which appeared to be principally n-octane, as determined by infrared and mass spectral analysis. The aqueous solution was submitted for analysis as described above.

E. REACTION OF TERT-BUTYLDIFLUORAMINE WITH NITRIC ACID

Concentrated nitric acid (10 ml, 0.15 mole) was added dropwise to 0.55 g (5.0 mmoles) of tert-butyldifluoramine under nitrogen at one atmosphere pressure. A very slight temperature rise was indicated by the passage of a few bubbles through a bubbler tube attached in series with a U-trap kept in a bath at -78°C. The mixture was stirred for two hours at room temperature and for 1-1/2 hours at 48-50°C. There was no indication that reaction occurred. After standing at room temperature for an additional 20 hours, the solution had become yellow and the gas phase had become brown. The material collected in the trap was expanded at 0°C into an infrared cell. Only a small amount of tert-butyldifluoramine was detected. The aqueous solution was then diluted with water and extracted twice with CCl_4. The infrared spectrum of

CCl_4 extract was compared with that of a sample of CCl_4 which had been treated with N_2O_4 in HNO_3. Extra absorptions in the extract of the reaction mixture were attributed to C-H (3.40/7.69 μ) and alkyl nitrite (6.11/7.79 μ). Evaporation of the aqueous HNO_3 solution left a very small residue of unidentified salt.

In a second experiment, 1.02 g (9.3 mmoles) of tert-butyldifluoramine was condensed under vacuum into a flask containing 10 ml (0.15 mole) of concentrated HNO_3. The mixture was warmed to room temperature and stirred. The pressure rose to 210-220 mm and remained constant for 16 hours. After this period, the pressure rose within 1-1/2 hours to 730 mm, with the evolution of brown gas. On cooling the reaction flask to -70°C, the pressure dropped to 340 mm. A sample of this gas was subjected to infrared analysis and found to contain C-H (3.33/6.75 μ), C-CH_3 (7.27 μ), N_2O (4.5 μ), N_2O_4 (5.72/6.15 μ), N-F (attributed to starting material, 10.30/11.35 μ), NO_3F (10.85/12.65/13.90 μ), CO_2 (4.35/15.96 μ), SiF_4 (9.75 μ), and NOCl (presumable from attack on NaCl window, 5.53/5.58 μ). Mass spectrometric analysis confirmed the presence of starting difluoramine, CO_2 and/or N_2O, SiF_4, and NO_3F, and established the absence of H_2 and O_2. A second gas sample taken at 0°C was found to contain some of these components, but no additional products. The acid solution was extracted with pentane to remove organic products. Infrared analysis of this extract revealed the presence of alkyl nitrite and nitrate (C-H at 3.51/6.90 μ, possible C-CH_3 at 7.28 μ, C-ONO at 6.41 μ, and C-ONO_2 at 6.10 μ). Analysis of the remaining aqueous phase is in progress.

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IV. FUTURE PLANS

During the next quarter, the following activities are planned:

-   Studies on the reaction of tert-butyldifluoramine with organo-
    metallic compounds and other one-electron reducing agents will
    be extended to include:

    ●   The effect of variations in mole ratio of reactants.
    ●   The effect of reversing the order of addition.

-   The reaction of tert-butyldifluoramine with nitric acid will be
    explored in greater detail, with particular emphasis on the
    stoichiometry and possible mechanisms for the reaction.

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Project 076
Report RMD-AOR-Q1-63

Section II

RMD Project 5007

(U)
SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

Section II

(U)
SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby

Report RMD-AOR-Q1-63

RMD Project 5007

Report Period: 15 December 1962

31 March 1963

Contract No. NOnr 3664(00)

ARPA Order No. 23-62

Project Code 3910

FOREWORD

This section of the quarterly report describes work conducted during the period from 15 December 1962 to 31 March 1963, on the synthesis of organic difluoramines for use in the study of structure-sensitivity relationships (RMD Project 5007).

The following technical personnel participated in this research: D. D. Perry (Project Scientist), A. P. Kotloby (Principal Investigator), J. A. Castellano (Synthesis), R. N. Storey, D. Y. Yee, and J. A. Creatura (Instrumental and Wet Chemical Analysis).

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ABSTRACT

Work is reported on the preparation of aliphatic vicinal and geminal difluoramines for use in evaluating relationships between structure and sensitivity in the organic difluoramines. Compounds having carbon to NF_2 ratios of 3:1 or less, and which are solids or liquids boiling above 56°C, are desired for this study.

During the current report period, the following compounds were prepared, purified and submitted to the Naval Ordnance Laboratory for sensitivity evaluation: 2,2-bis(difluoramino)pentane, 1,1-bis(difluoramino)cyclopentane, 1,2-bis(difluoramino)cyclohexane, and 1,1-bis(difluoramino)cyclohexane. These compounds are stable, distillable liquids and are shock sensitive in qualitative tests.

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Project 5007
Report RMD-AOR-Q1-63

I. INTRODUCTION

Investigations of organic difluoramines as ingredients of rocket propellants have produced a large variety of poly(difluoramino) compounds. A common feature of these compounds is their sensitivity to impact. Since propellants are normally subjected to many kinds of stresses during handling, storage and use, the study of the impact and thermal sensitivity of difluoramino compounds is important in assessing their practical value as propellants.

In order to determine whether systematic relationships between the structure and sensitivity of this class of compounds can be established, the Reaction Motors Division of Thiokol Chemical Corporation has undertaken a program sponsored by the Advanced Research Projects Agency and the Office of Naval Research for the preparation of a series of organic difluoramines for sensitivity evaluation. The preparation and purification of the compounds are the responsibility of Reaction Motors Division, while sensitivity tests are conducted at the Naval Ordnance Laboratory, White Oak, Maryland.

II. DISCUSSION

Previous efforts on this program were centered on the preparation of poly(difluoramino) carbamates (Ref 1), since these materials were expected to be low-melting solids and could, therefore, be evaluated in both the Bureau of Mines dropweight test (Ref 2) and the thermal explosion delay test (Ref 3).

As expected, the sensitivity of the carbamates as measured by the explosion delay test was found to increase with a decrease in the $C:NF_2$ ratio. It appeared that when the $C:NF_2$ ratio was greater than three, results in this test were not significant because of the long delay to the explosion causing erratic results. It was also found that the low energy carbamate group further reduced the impact sensitivity of these compounds. Furthermore, improvements in the accuracy of the explosion delay test, which employs liquids, made this test of greater interest in the study. Therefore, it was decided that further synthetic work would be limited to compounds with $C:NF_2$ ratio of three or less and that no special effort would be made to prepare solids. Organic difluoramines having functional groups likely to be employed in propellant compounds have been selected, and structural variations are being sought which will permit correlation of the sensitivity with the following factors:

- Oxidative balance of the molecule

- Normal versus branched chain and cyclic structures at a given $C:NF_2$ ratio, and with both geminal and vicinal NF_2-groups

- Other functional group(s) in the organic difluoramine molecule

Below are listed in the order of decreasing emphasis the types of compounds (containing both vicinal or geminal NF_2-groups) that are to be synthesized on this program:

1) Alkanes, cyclic and acyclic
2) Alkenes, cyclic and acyclic
3) Esters
4) Acetals
5) Ethers

6) Nitriles
7) Alcohols
8) Ketones
9) Halides
10) Nitro compounds
11) Perfluoro and partially fluorinated hydrocarbons

A. PREPARATION OF VICINAL DIFLUORAMINES

The addition of tetrafluorohydrazine to olefins is a general route for the synthesis of vicinal bis(difluoramines). In the case of unhindered olefins containing isolated double bonds, the reaction can usually be carried out at approximately atmospheric pressure in a glass bulb. For volatile or somewhat less reactive olefins, the reaction is conveniently carried out in an all-glass pressure reactor of the Fischer-Porter type (Ref 4), or in steel Hoke bomb, at 70-100°C under a pressure of 150-250 psig. In order to form tetrakis-NF_2 adducts from conjugated dienes, higher temperatures and pressures and longer reaction time are generally required (Ref 5). In a typical reaction, a solution of the olefin in a solvent (e.g., Freon-113) is charged into the pressure reactor and degassed at -80°C The solvent moderates the reaction and also desensitizes the reaction products. Tetrafluorohydrazine is then condensed into the reactor at -196°C, and the contents are heated for a period of 3-24 hours. The yield of crude product is usually in the range of 60-80% of the theoretical yield.

During the current report period, work on the preparation of vicinal bis(difluoramines) was limited to the preparation of 1,2-bis(difluoramino)-cyclohexane, prepared previously on another program (Ref 6). The procedure described in this reference was used, and a 45% yield was obtained.

B. PREPARATION OF GEMINAL DIFLUORAMINES

The reaction of carbonyl compounds with HNF_2 in ~100%-H_2SO_4 to yield geminal bis(difluoramines) has been investigated in many laboratories (e.g., Ref 7). At present, the best source of HNF_2 required for this reaction is N,N-difluorourea, from which difluoramine is readily generated by acid hydrolysis (Ref 8, 9). Both reactions, the fluorination of urea and the generation of HNF_2, proceed smoothly and in high yields. After being scrupulously dried, the difluoramine is refluxed in ~100%-H_2SO_4 (or SO_3), and a methylene chloride solution of the ketone or aldehyde is added. Experimental conditions are critical. Failure to use acid of sufficient strength or use of too

small a quantity of acid results in failure of the reaction. Too much acid and/or too long a reaction time drastically reduce the yield. In general, the specific reaction conditions must be worked out for each new compound. Once prepared, geminal organodifluoramines are readily purified by distillation. Work with compounds having a high NF_2/C ratio must be carried out in a shielded hood and on small scale, owing to their high-impact sensitivity.

During this period, 1,1-bis(difluoramino)cyclopentane, 1,1-bis(difluoramino)-cyclohexane and 2,2-bis(difluoramino)pentane were prepared. Details of these preparations will be found in the Experimental Section.

III. EXPERIMENTAL

A. PREPARATION OF DIFLUOROUREA BY AQUEOUS FLUORINATION

A 1000-ml three-neck flask was filled with a solution of 50 g (0.83 mole) of urea in 600 ml of water. The solution was cooled to 0°C by means of an external ice-water bath. A 20% (by volume) mixture of fluorine in nitrogen was bubbled through the vigorously stirred solution, the temperature of which was kept at 0-5°C. Over a period of six hours, 2.0 moles of fluorine were bubbled through the solution. The solution was then stirred for an additional hour under a stream of nitrogen. The total volume of solution at the end of the reaction was 670 ml, indicating an increase in volume of 70 ml. The titration of the solution (iodometric method) showed the presence of 4.032 meq/ml of difluoramine. The yield of N,N-difluorourea was 64.8 g (0.675 mole, 70%). In order to avoid the detrimental effect of glass on aqueous difluorourea (Ref 5), the solution was stored in polyethylene containers.

B. SYNTHESIS OF 2,2-BIS(DIFLUORAMINO)PENTANE

2-Pentanone (1.00 g, 0.012 mole), bp 102.4°C, was dissolved in 3 ml of dichloromethane and gradually added to a stirred mixture of 101.4% H_2SO_4 (20 ml) and difluoramine (1.06 g, 0.02 mole) kept under reflux at -80°C. The HNF_2 was generated by hydrolysis of 73.5% aqueous solution of N,N-difluorourea in the presence of 40 ml of conc H_2SO_4. A general view of the HNF_2 generator and reactor is shown in Figure 1.

After the addition of HNF_2 was completed, the reactants were stirred for four more hours. At the end of this period, the -80°C condenser had come to room temperature due to evaporation of the Dry Ice. The reaction mixture was extracted with dichloromethane. The organic layer was washed with aqueous $NaHCO_3$, then with distilled water until it was neutral, and dried over anhydrous $MgSO_4$. The filtered solution was freed off the solvent by evaporation, and the residue was distilled from Aroclor 1242*(bp 325-366°C) solution under reduced pressure. The use of high-boiling solvent permitted the complete distillation of the product without much loss on the walls of the flask and without decomposition of the residue. The 2,2-bis(difluoramino)-pentane obtained is a pungent, moderately impact-sensitive, colorless liquid (1.32 g, 63.4% yield), bp 44.0-45.0°C/19.0 mm Hg, n_D^{25} 1.3701. Its infrared

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*Monsanto Chemical Co., Organic Chemicals Division, St. Louis, Missouri
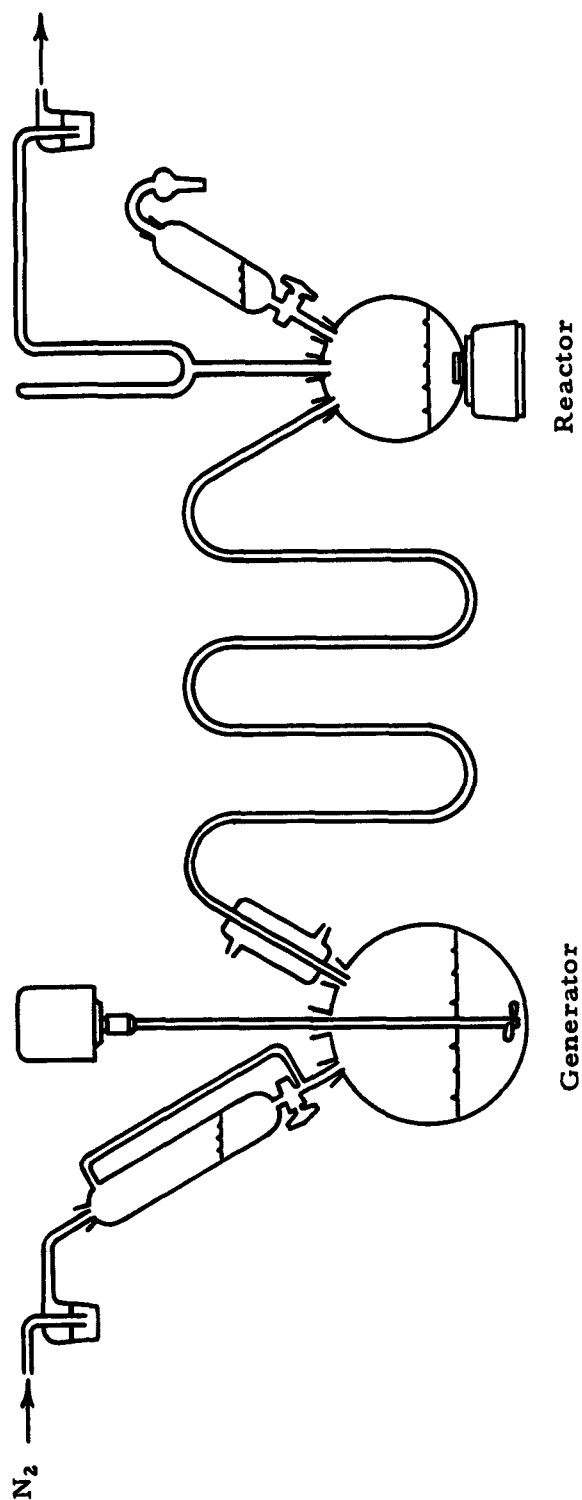
Figure 1. HNF$_2$ Generator and Reactor

spectrum contained characteristic absorptions of the NF_2-group (10.1, 10.2, 11.1, 11.2, 11.6 μ) and C-H absorptions.

Anal. Calcd. for $C_5F_4H_{10}N_2$: C, 34.49; H, 5.79 N, 16.09. Found: C, 35.13; H, 6.22; N, 15.93.

C. PREPARATION OF 1,1-BIS(DIFLUORAMINO)CYCLOHEXANE

Into a 500-ml three-neck flask fitted with a water condenser and a dropping funnel was placed 100 ml of 4N N,N-difluorourea solution. Into the stirred solution, 25 ml of conc H_2SO_4 was added dropwise under a stream of nitrogen. After the addition, the solution was heated to 90°C for one hour. The gases generated (CO_2 and HNF_2) were passed through a water-cooled condenser, a 0°C trap, and a tube filled with anhydrous $CaSO_4$. The dry gas mixture was then passed into a 100-ml three-neck flask containing 30 ml of 100.6%-H_2SO_4 and fitted with a -80°C cendenser and an addition funnel. When refluxing of HNF_2 became apparent, a solution of 0.010 mole of cyclohexanone in 1 ml of CH_2Cl_2 was added dropwise to the stirred H_2SO_4-HNF_2. The rate of reflux in the reaction flask decreased as the reaction proceeded. After about three hours, 20 ml of CH_2Cl_2 was added to the reaction flask, and the product was separated, followed by $NaHCO_3$ and water washings. After purification by distillation, 1.87 g (50% yield), of 1,1-bis(difluoramino)cyclohexane, bp 50.0-50.5°C/10.0 mm, n_D^{25} 1.4080, was obtained.

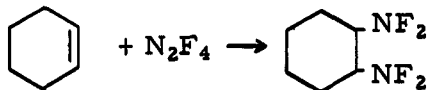Anal. Calcd. for $C_6F_4H_{10}N_2$: C, 38.71; H, 5.41; N, 15.05. Found: C, 39.02; H, 4.48; N, 15.18.

D. SYNTHESIS OF 1,1-BIS(DIFLUORAMINO)CYCLOPENTANE

Difluoramine was generated in the same way as in the reaction described above and passed into 5 ml of 101.6%-H_2SO_4, to which was gradually added 1.2 g (0.014 mole) of cyclopentanone in 3 ml of CH_2Cl_2. Work-up of the mixture gave 2.0 g (0.012 mole, 81% yield) of 1,1-bis(difluoramino)cyclopentane, bp 60.0-60.5°C/60.0 mm.

Anal. Calcd. for $C_5F_4H_8N_2$: C, 34.89; H, 4.68; N, 16.17. Found: C, 34.66; H, 4.47; N, 15.82.

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E. SYNTHESIS OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

This reaction was run according to the previously described procedure (Ref 6). The purified 1,2-bis(difluoramino)cyclohexane (cis-trans mixture), bp 40.0-41.0°C/5.0 mm, n_D^{25} 1.4123, was obtained in 45% yield.

Anal. Calcd. for $C_6F_4H_{10}N_2$: C, 38.71; F, 40.82; H, 5.41; N, 15.05.
Found: C, 38.00; F, 39.40; H, 4.48; N, 14.60.

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V. FUTURE WORK

During the next period we plan to continue work on the synthesis of difluoramino hydrocarbons, and extend the work to NF_2 derivatives containing ester, ether, keto, and nitrile groups.

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V. REFERENCES

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Section III

RMD Project 5017

(U)
STABILIZATION OF HIGH ENERGY SOLID OXIDIZER

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Section III

(U)
STABILIZATION OF HIGH ENERGY SOLID OXIDIZER

A. R. Young
J. Dvorak

Report RMD-AOR-Q1-63

RMD Project 5017
Report Period: 1 November 1962 to
31 March 1963

Contract No. NOnr 3913(00)
ARPA Order No. 354-62
Project Code 2910

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FOREWORD

This section of the report summarizes the work carried out during the period from 1 November 1962 to 31 March 1963, on the chemical stabilization of nitronium perchlorate (RMD Project 5017).

Contributors to the research described during the report period are as follows: A. R. Young (Project Supervisor), J. Dvorak (Principal Investigator), D. Yee (Mass Spectroscopy), E. Egbert (X-ray Analysis), J. Creatura (Wet Chemical Analysis).

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ABSTRACT

The following compounds have been examined as potential nitronium ion ligands: NOCl, NO, NOF, $(CH_3)_3N$, and N_2F_2. None of these reagents form stable coordination complexes with nitronium perchlorate. However, as a result of studies of the reactions of NOCl, NO, and NOF with NO_2ClO_4 and with NO_2BF_4, strong evidence has been obtained for the existence of a new "nitroxy" cation, $N_2O_3^{+2}$. The compound $N_2O_3(BF_4)_2$ has been characterized by chemical, x-ray, and thermal analysis. It is believed that the corresponding perchlorate, $N_2O_3(ClO_4)_2$ has been synthesized as well, but characterization is not as yet complete.

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I. INTRODUCTION

The objective of this program is to improve the physical and chemical properties of nitronium perchlorate by coordinating ligand molecules to the nitronium ion. During this report period, the following compounds have been examined as potential nitronium ion ligands: $NOCl$, NO, NOF, $(CH_3)_3N$, and N_2F_2. No evidence for formation of a stable nitronium ion complex has been obtained in these experiments. However, considerable evidence has been found for the existence of stable fluoroborate and perchlorate salts of a new "nitroxy" cation, $N_2O_3^{+2}$. The thermal stability of $N_2O_3(BF_4)_2$ is markedly greater than that of NO_2BF_4. Sufficiently pure $N_2O_3(ClO_4)_2$ has not as yet been obtained to permit studies of its physical properties in comparison to NO_2ClO_4, but $N_2O_3(ClO_4)_2$ behavior is expected to parallel that of $N_2O_3(BF_4)_2$.

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II. DISCUSSION

Two approaches have been pursued in an attempt to synthesize a stable complex of nitronium perchlorate.

The first approach involves the formation of a complex nitronium cation associated with an anion other than perchlorate and subsequent conversion to a complex nitronium perchlorate by metathesis. Studies made with nitronium fluoroborate are illustrative of this method.

The second approach involves investigation of direct reactions of nitronium perchlorate with potential ligands such as NO, NOF, N_2F_2, NH_3, and N_2H_4. The principal effort during this report period was devoted to the latter approach.

A. PREPARATION OF THE COMPLEX SALT, $N_2O_3(BF_4)_2$

Solutions of nitrosyl salts have been reported to yield the complex cation, $N_2O_3^{+2}$, when treated with NO_2 (Ref 1). Preliminary attempts to demonstrate the existence of this cation in the solid state involved the reaction of $NOBF_4$ with NO_2 (Ref 2). Subsequent attempts to prepare the $N_2O_3^{+2}$ cation by the reaction of NO_2BF_4 with NO resulted in the isolation of a new complex salt, $N_2O_3(BF_4)_2$ via the reaction shown in equation 1.

$$2NO_2BF_4 + NO \longrightarrow N_2O_3(BF_4)_2 + NO_2 \tag{1}$$
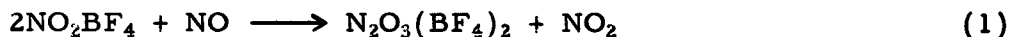
Thermal decomposition of $N_2O_3(BF_4)_2$ gives rise to equimolar amounts of NO and NO_2 as determined by mass spectroscopic analysis. Boron trifluoride is also present in the decomposition gases. Determination of boron by standard wet chemical analysis on samples of $N_2O_3(BF_4)_2$ from two separate preparations gave values of 8.36 and 8.61%, respectively. These compare favorably with the calculated value of 8.64%. The 2:1 stoichiometry suggested in equation 1 is established by the fact that one mole of NO is completely consumed by two moles of NO_2BF_4. This process can be followed visually by noting the gradual disappearance (at low temperatures) of a blue color due to N_2O_3. If at this point additional NO is added to the system, the blue color of N_2O_3 becomes permanent, showing that no more NO is being consumed.

The reaction product, $N_2O_3(BF_4)_2$, is distinguished from an equimolar mixture of $NOBF_4$ and NO_2BF_4 by its insolubility in acetonitrile. Addition of NO to a solution of NO_2BF_4 in acetonitrile results in the precipitation of $N_2O_3(BF_4)_2$. Differences in the thermal decomposition temperatures which have been observed for $N_2O_3(BF_4)_2$ and an equimolar mixture of $NOBF_4$ and NO_2BF_4 when measured in standard melting point capillaries serve as additional evidence the $N_2O_3(BF_4)_2$ is not a mixture (Table I). A comparison of the x-ray powder patterns of $N_2O_3(BF_4)_2$ and an equimolar mixture of NO_2BF_4 and $NOBF_4$ also substantiates the claim that $N_2O_3(BF_4)_2$ is a true compound (Figure 1).

TABLE I

THERMAL DECOMPOSITION TEMPERATURES OF VARIOUS FLUOROBORATES

NO_2BF_4	$NOBF_4$	Equimolar Mixture of $NOBF_4$ and NO_2BF_4	$N_2O_3(BF_4)_2$
---	---	---	---
135°C	130°C	125°C	295°C

It is interesting to note that a reaction of $N_2O_4 \cdot 2BF_3$ with H_2SO_4 (equation 2) has been reported to yield an equimolar mixture of nitrosyl and nitryl tetrafluoroborates (Ref ?).

$$N_2O_4 \cdot 2BF_3 \xrightarrow{\ H_2SO_4\ } NOBF_4 + NO_2BF_4 + \cdots \cdot \qquad (2)$$
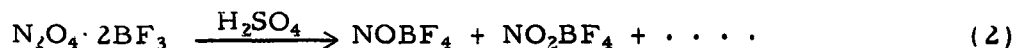
However, it is pointed out by the author that the x-ray pattern of the material does not show the major lines of NO_2BF_4. A comparison of the diffraction patterns of the $N_2O_4 \cdot 2BF_3 - H_2SO_4$ product with that of $N_2O_3(BF_4)_2$ shows that they are nearly identical (Figure 2). It is possible, therefore, that $N_2O_3(BF_4)_2$ may be prepared by the reaction of N_2O_4 with BF_3 in H_2SO_4.

B. REACTION OF $N_2O_3(BF_4)_2$ WITH NH_4ClO_4

An attempt was made to prepare a new complex perchlorate by utilizing $N_2O_3(BF_4)_2$ (equation 3).

$$N_2O_3(BF_4)_2 + 2NH_4ClO_4 \xrightarrow{\quad} N_2O_3(ClO_4)_2 + 2NH_4BF_4 \qquad (3)$$

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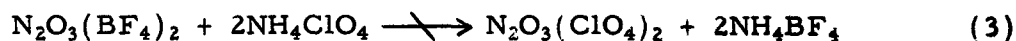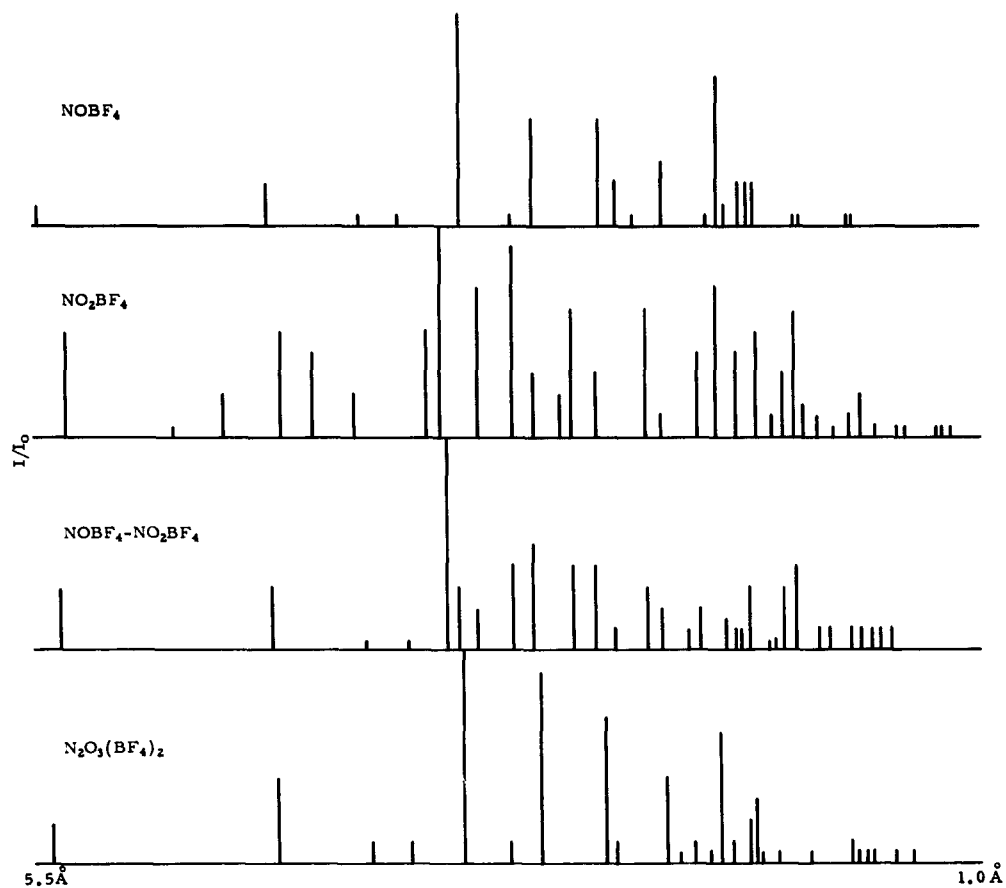
Figure 1. Diffraction Patterns of Fluoroborates
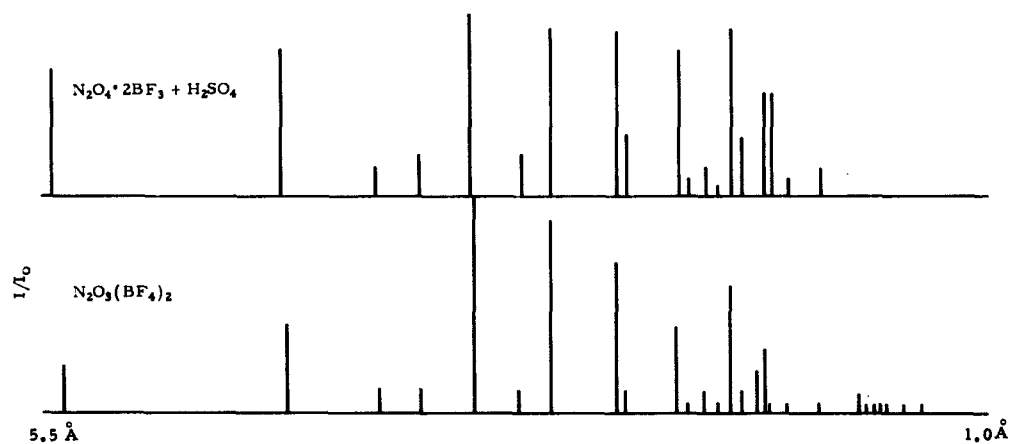
Figure 2. Diffraction Pattern of $N_2O_3(BF_4)_2$

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A single experiment was conducted in which $N_2O_3(BF_4)_2$ and NH_4ClO_4 were allowed to react in liquid HF. A small amount of NO and NO_2 was liberated, but there was no indication that the desired reaction occurred.

C. REACTION OF TRIMETHYLAMINE WITH NO_2^+

An attempt was made to prepare a complex nitronium cation by the reaction of NO_2BF_4 with $N(CH_3)_3$ (equation 4).

$$NO_2BF_4 + N(CH_3)_3 \xrightarrow{\quad} NO_2\left[N(CH_3)_3\right]BF_4 \qquad (4)$$
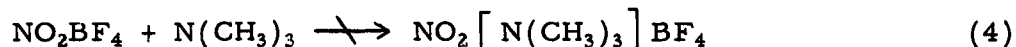
When $N(CH_3)_3$ was added to a solution of NO_2BF_4 in acetonitrile, a vigorous reaction ensued, and N_2, N_2O, NO and NO_2 were evolved. The solid product obtained after removal of the acetonitrile gave a negative test for nitrite and nitrate ions. Trimethylamine is evolved upon basic hydrolysis. The product is believed to be $(CH_3)_3N{:}BF_3$. Analysis of the solid is given in Table II.

TABLE II

ANALYSIS OF THE NO_2BF_4-$N(CH_3)_3$ REACTION PRODUCT

Atom	Calcd. for $(CH_3)_3N{:}BF_3$ (%)	Found (%)
C	28.39	23.97
H	7.09	7.07
N	11.04	9.05
B	8.51	8.42

D. REACTION OF NO_2ClO_4 WITH NOCl

The reaction of NO_2ClO_4 with excess NOCl has been reported (Ref 2). Analysis of the product, including the x-ray diffraction pattern, suggested that the $N_2O_3^{+2}$ cation was present (equation 5).

$$2NO_2ClO_4 + NOCl \longrightarrow N_2O_3(ClO_4)_2 + NO_2Cl \qquad (5)$$

Peculiar color changes were previously observed when nitromethane was added to the solid reaction product. It has since been determined that some NO and

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NO_2 are evolved upon treatment with nitromethane. However, the solid recovered from the nitromethane solution has an x-ray powder pattern consistent with that of the solid before addition of nitromethane (Figure 3), indicating that only partial decomposition occurs. The gas evolution in nitromethane has subsequently been avoided by scrupulously drying the solvent.

In an attempt to define the stoichiometry of the reaction of NO_2ClO_4 with NOCl, several experiments were conducted in which the mole ratio of NO_2ClO_4 to NOCl was 2:1. In each reaction NO_2Cl was evolved. However, on the basis of x-ray patterns, the solid products obtained varied in composition from run to run. In one of these experiments, NOCl was added to a solution of NO_2ClO_4 in nitromethane in order to obtain more efficient mixing, and the product was isolated by distillation of the solvent in vacuo. The x-ray powder pattern of the product was different than those previously obtained for NO_2ClO_4-NOCl reaction products when excess NOCl was used (Figure 4). It is presently believed that the discrepancies noted in the various x-ray diffraction patterns are either the result of inefficient mixing of the NOCl with NO_2ClO_4 or the failure to allow sufficient time for complete reaction.

It is interesting to note that chemical analysis of a representative sample gives a mole ratio of NO/NO_2 which is approximately unity (Table III).

TABLE III

ANALYSIS OF NO_2ClO_4-1/2 NOCl REACTION PRODUCT

Group	Calcd. for $N_2O_3(ClO_4)_2$ (%)	Found (%)
NO	10.9	7.7
NO_2	16.7	11.8
ClO_4	72.6	66.1

E. REACTION OF NO_2ClO_4 WITH NO

It has been determined that excess NO reacts with NO_2ClO_4 to yield a white solid (equation 6), identical to that obtained when NO_2ClO_4 is allowed to react with excess NOCl.

$$2NO_2ClO_4 + NO \longrightarrow N_2O_3(ClO_4)_2 + NO_2 \qquad (6)$$

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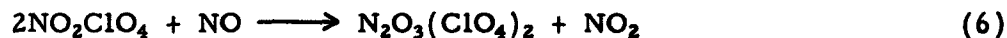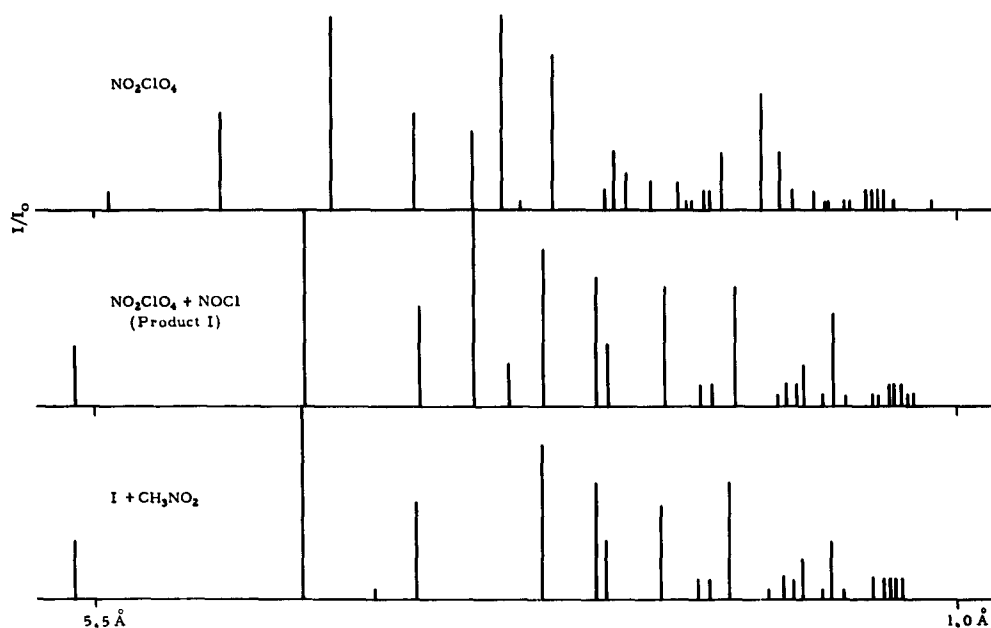
Figure 3. Diffraction Patterns of NO_2ClO_4-NOCl Reaction Products (Part I)
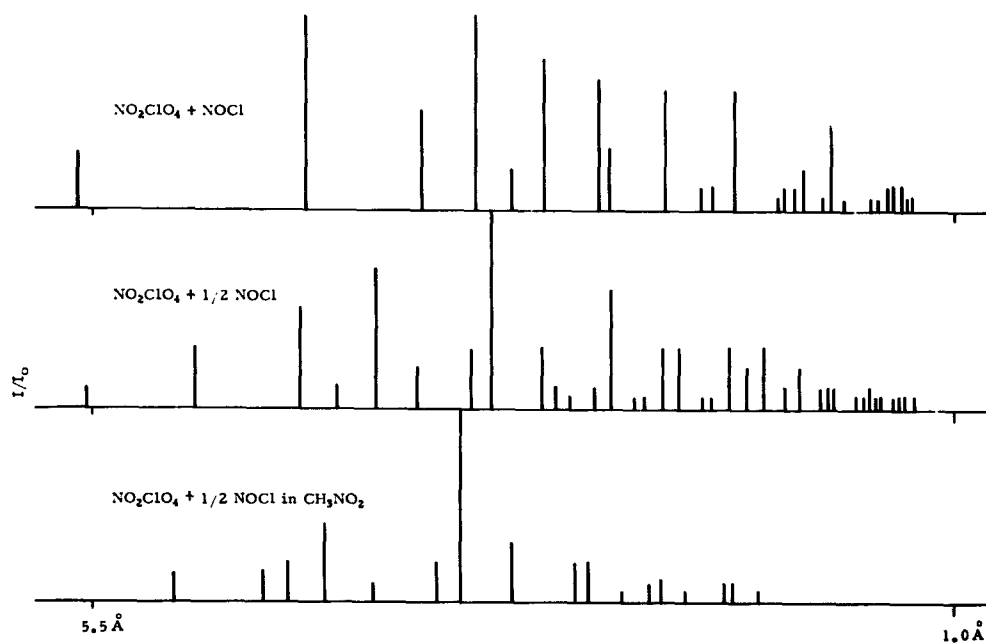
Figure 4. Diffraction Patterns of NO_2ClO_4-NOCl Reaction Products (Part II)

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Analysis of the product resulted in an NO/NO_2 ratio of approximately unity (Table IV).

TABLE IV

ANALYSIS OF NO_2ClO_4-NO REACTION PRODUCT

Group	Calcd. for $N_2O_3(ClO_4)_2$ (%)	Found (%)
NO	10.9	7.8
NO_2	16.7	13.0
ClO_4	72.6	75.7

Similar results are obtained when NO is allowed to react with a suspension of NO_2ClO_4 in liquid NO_2. A comparison of the x-ray powder patterns of those products is given in Figure 5.

When NO was condensed on NO_2ClO_4 in the mole ratio of 1:2, the white solid obtained gave an x-ray powder pattern inconsistent with prior results. However, when the reaction was conducted in nitromethane or liquid SO_2, using the same NO_2ClO_4 to NO molar ratio, the products obtained had x-ray powder patterns similar to those of products obtained when excess NO or excess NOCl were used (Figure 6).

F. REACTION OF NO_2ClO_4 WITH NOF

The reaction of NOF with NO_2ClO_4 was examined to determine if NOF might react differently than NOCl and produce a complex having NOF as a ligand group. In a preliminary experiment, commercially available NOF was employed. Subsequent experiments were conducted with freshly prepared NOF to preclude any possibility of reaction with an NO impurity. The NOF was generated in situ by the reaction of NOCl with HF (equations 7, 8).

$$NOCl + HF \longrightarrow NOF + HCl \uparrow \qquad (7)$$

$$2NO_2ClO_4 + NOF \longrightarrow N_2O_3(ClO_4)_2 + NO_2F \qquad (8)$$
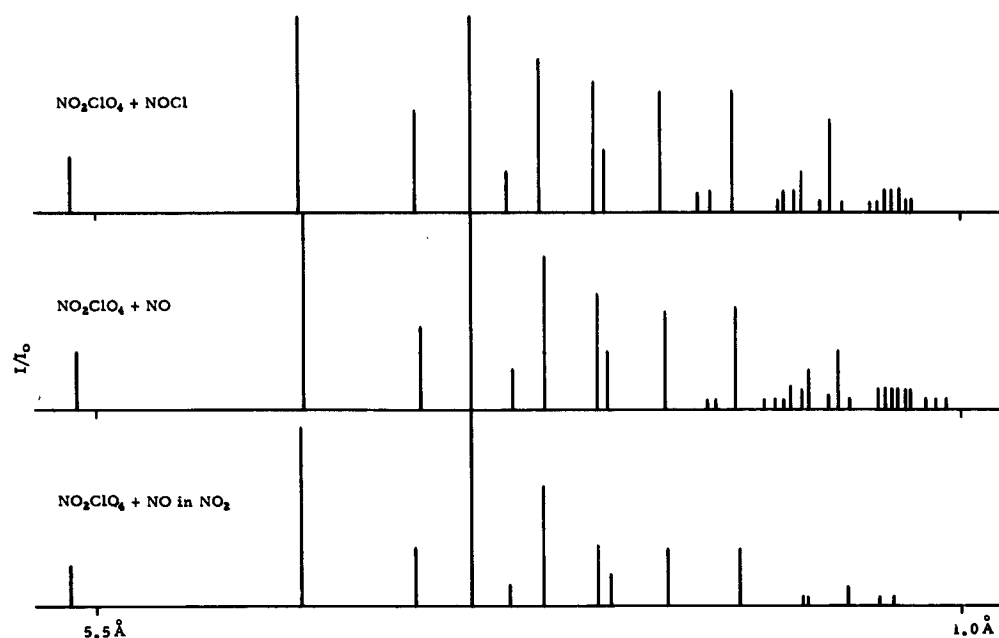
Figure 5. Diffraction Patterns of NO_2ClO_4-NO Reaction Products
(Part I)
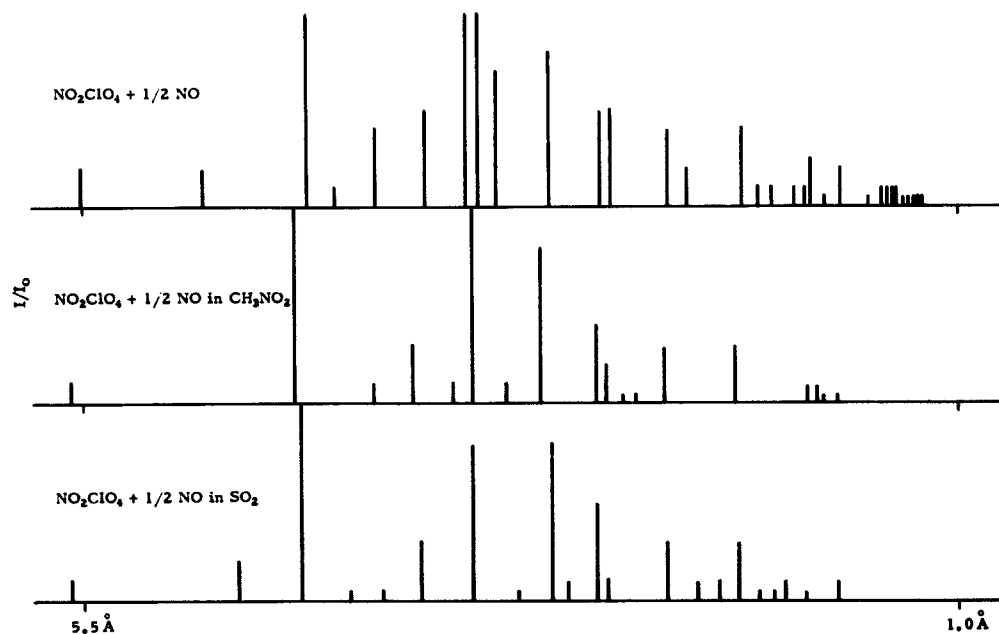
Figure 6. Diffraction Patterns of NO_2ClO_4-NO Reaction Products
(Part II)

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In the initial run carried out in HF, the solid gave a different x-ray pattern (Figure 7) than the NO$_2$ClO$_4$-NOCl product, and it was thought that it might be NO$_2$ClO$_4 \cdot$ NOF. However, the product gave a negative test for fluoride. The solid obtained in the second run gave an x-ray pattern identical to that of the NO$_2$ClO$_4$-NOCl product. It was concluded that NOF reacts with NO$_2$ClO$_4$ in the same manner as NOCl.

G. REACTION OF NO$_2$ClO$_4$ WITH CIS-N$_2$F$_2$

An attempt was made to prepare a complex perchlorate by the reaction of cis-N$_2$F$_2$ with NO$_2$ClO$_4$ (equation 9). However, no reaction occurred between NO$_2$ClO$_4$ and gaseous or liquid cis-N$_2$F$_2$. Both reagents were recovered.

$$NO_2ClO_4 + N_2F_2 \xrightarrow{\hspace{0.3cm}\backslash\hspace{0.3cm}} NO_2/N_2F_2/ClO_4 \tag{9}$$
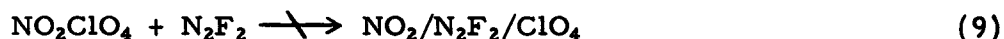
H. REACTION OF N$_2$O$_3$(ClO$_4$)$_2$ WITH NO$_2$BF$_4$

The reactions of NO, NOCl and NOF with NO$_2$ClO$_4$ in most instances yielded the same product as shown by x-ray analysis. The mole ratio of NO/NO$_2$ in these products is approximately unity. Therefore, the formation of a salt, N$_2$O$_3$(ClO$_4$)$_2$, analogous to the complex fluoroborate, N$_2$O$_3$(BF$_4$)$_2$, is strongly indicated. A definitive proof that we are dealing with a compound, and not an equimolar mixture of NOClO$_4$ and NO$_2$ClO$_4$, remains to be given.

A very convenient proof would be to prepare N$_2$O$_3$(BF$_4$)$_2$ from the NO$_2$ClO$_4$-NO product. Fortunately NO$_2$ClO$_4$, NO$_2$BF$_4$ and the NO$_2$ClO$_4$-NO product are all soluble in acetonitrile, so that the reaction shown in equation 10 appears to be a reasonable method of preparation for N$_2$O$_3$(BF$_4$)$_2$.

$$N_2O_3(ClO_4)_2 + 2NO_2BF_4 \xrightarrow{CH_3CN} N_2O_3(BF_4)_2\downarrow + 2NO_2ClO_4 \tag{10}$$
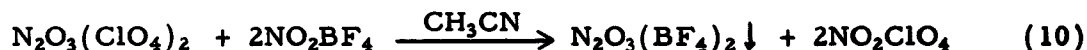
A preliminary attempt was, therefore, made to carry out this reaction. The addition of an acetonitrile solution of N$_2$O$_3$(ClO$_4$)$_2$ resulted in evolution of NO and NO$_2$ accompanied by what appeared to be extensive decomposition. No precipitation occurred.

It is believed that the NO$_2$BF$_4$ contained moisture and the gassing was due to a reaction with this impurity. An attempt will be made to carry out this reaction under scrupulously dry conditions.

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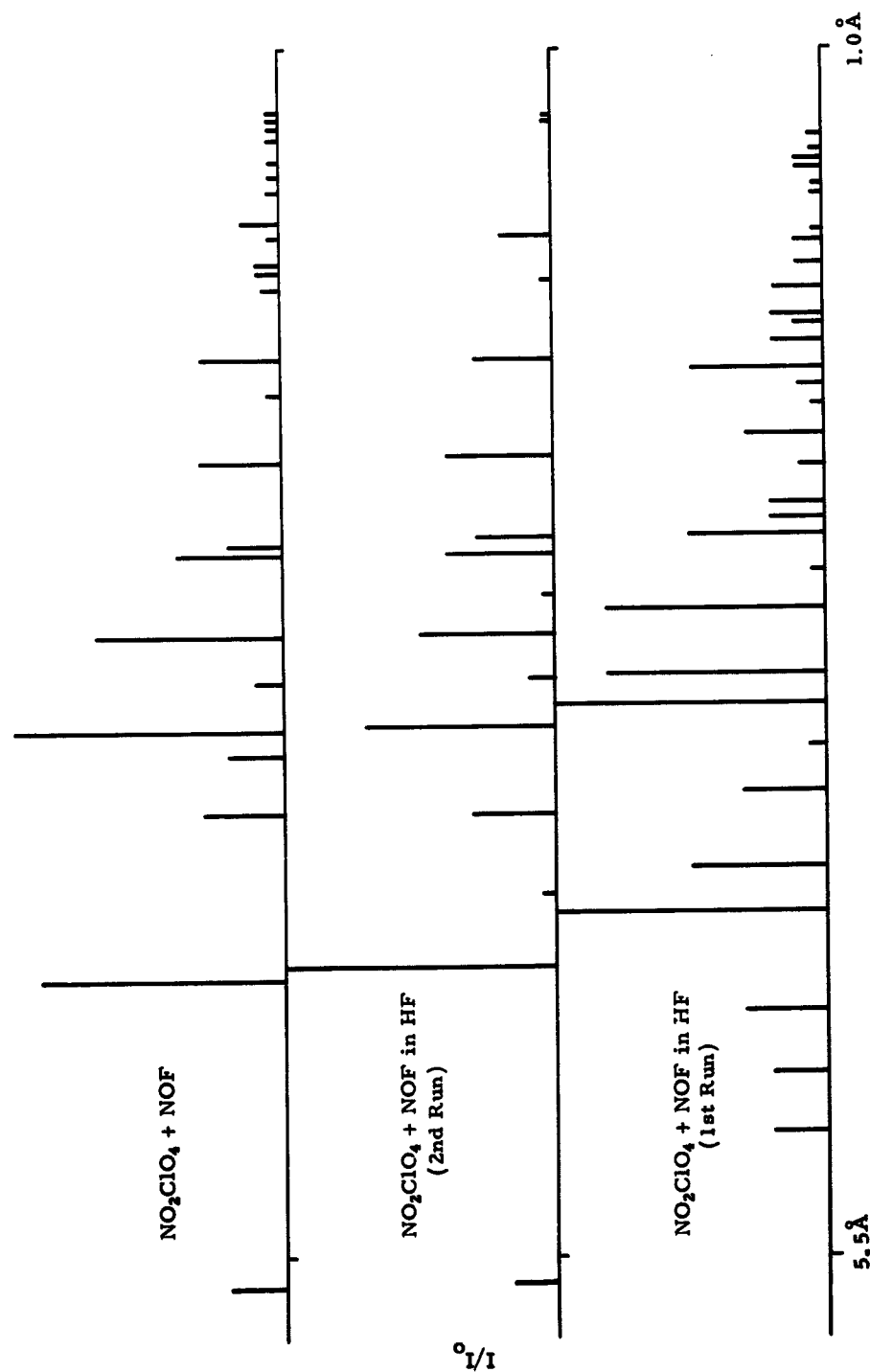
Figure 7. Diffraction Patterns of NO_2ClO_4-NOF Reaction Products

NO_2ClO_4 + NOF

NO_2ClO_4 + NOF in HF
(2nd Run)

NO_2ClO_4 + NOF in HF
(1st Run)

$^{\circ}I/I$

5.5Å

1.0Å

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I. REACTION OF NO_2ClO_4 WITH SULFOLANE

Nitronium perchlorate was found to dissolve readily in Sulfolane (tetramethylene sulfone). Addition of chloroform, essentially a nonsolvent, did not result in precipitation of NO_2ClO_4. The solution after hydrolysis gave a positive test for ClO_4^- with ϕ_4AsCl but a negative brown ring test for NO_3^-. Consequently, the reaction was repeated by adding an equimolar amount of Sulfolane to a suspension of NO_2ClO_4 in $CHCl_3$. Only a trace of solid remained. It was separated by filtration, and x-ray analysis is pending. The filtrate was hydrolyzed and gave a positive test for ClO_4^- but a negative test for NO_3^-. The nature of this reaction is not presently understood.

III. EXPERIMENTAL

Most of the reactions described were conducted in Pyrex Fischer and Porter Aerosol Compatibility Tubes fitted with a pressure gauge, a metal valve, and a ball joint for connection to the vacuum line. Those reactions in which a solvent was present were carried out in round bottom flasks fitted with a sintered glass disk, stop-cock and ball joint. This assembly could be attached to the vacuum system and subsequently removed and inverted to filter the reaction mixture.

All sampling of solid reagents and preparation of solid products for x-ray analysis were carried out in a dry box.

A. PREPARATION OF THE COMPLEX SALT, $N_2O_3(BF_4)_2$

To a solution of 2.47 g (18.7 mmoles) of NO_2BF_4 in approximately 30 ml of acetonitrile was added, at -196°C, 9.3 mmoles of NO. The reaction mixture was allowed to warm to room temperature and was stirred for several hours. The precipitated product was separated by filtration. Characterization of the product was presented earlier in the Discussion Section.

The reaction was also conducted by condensing the NO on NO_2BF_4 at -196°C and allowing the reaction mixture to warm slowly to room temperature. The NO was kept in contact with the NO_2BF_4 by repetitive condensation. The reaction could be followed by determination of the composition of the gaseous fraction. The solid was washed with acetonitrile and dried in vacuo.

B. REACTION OF $N_2O_3(BF_4)_2$ WITH NH_4ClO_4

To a mixture of 0.768 g (3 mmole) of $N_2O_3(BF_4)_2$ and 1.416 g (12 mmoles) of NH_4ClO_4 in a Kel-F reactor was added 25 ml of liquid HF. The reaction mixture was allowed to stir several hours during which time some NO and NO_2 were evolved. The solid isolated after removal of the HF was insoluble in both nitromethane and acetonitrile. The desired product, $N_2O_3(ClO_4)_2$, is known to be soluble in these solvents.

C. REACTION OF NO_2BF_4 WITH $N(CH_3)_3$

To 0.936 g (7.0 mmoles) of NO_2BF_4 in 30 ml of acetonitrile was added, at $-196°C$, 7.0 mmoles of $N(CH_3)_3$. The reaction mixture was allowed to warm slowly to room temperature, and considerable gassing occurred. Mass spectroscopic analysis of the evolved gas showed the presence of N_2, N_2O, NO and NO_2. A wax-like solid, melting with decomposition in the range $180-185°C$, was obtained after removal of the solvent. Analysis of the solid was as follows:

Atom	Calcd. for $(CH_3)_3N{:}BF_3$ (%)	Found (%)
C	28.39	23.97
H	7.09	7.07
N	11.04	9.05
B	8.51	8.42

D. REACTION OF EXCESS NO_2ClO_4 WITH NOCl

The reaction of NO_2ClO_4 with excess NOCl has been described previously (Ref 2). The reaction was conducted similarly with NO_2ClO_4 in excess. To 0.660 g (4.55 mmoles) of NO_2ClO_4 at $-196°C$ was added 2.27 mmoles of NOCl. The reaction mixture was allowed to warm slowly and was stirred for several hours at $0°C$. The volatile fraction was removed by pumping on the solid. The solid was analyzed for NO^+ and NO_2^+ content after hydrolytic conversion of these cations to nitrite (NO_2^-) and nitrate (NO_3^-), respectively. The nitrite ion was titrated with standard ceric sulfate solution, and the nitrate was determined by treating an aliquot of the hydrolysate with excess standard ferrous sulfate followed by titration with standard ceric sulfate. The perchlorate anion was determined colorimetrically. The analysis gave the following results:

Group	Calcd. for $N_2O_3(ClO_4)_2$ (%)	Found (%)
NO	10.9	7.7
NO_2	16.7	11.8
ClO_4	72.6	66.1

This reaction has also been conducted by the addition of NOCl to a solution of NO_2ClO_4 in nitromethane. The reaction mixture was allowed to warm to room temperature and stirred for several hours. The solvent was removed by distillation in vacuo.

E. REACTION OF NO_2ClO_4 WITH NO

1. Excess NO

To 0.520 g (3.57 mmoles) of NO_2ClO_4 at -196°C was added 4.42 mmoles of NO. The reaction mixture was allowed to warm slowly to room temperature with stirring. The gas was recondensed on the solid several times. The system was then evacuated, and a white solid was obtained. The solid product was analyzed according to the method described in subsection D above. The results were as follows:

Group	Calcd. for $N_2O_3(ClO_4)_2$ (%)	Found (%)
NO	10.9	7.8
NO_2	16.7	13.0
ClOF	72.6	75.7

2. Excess NO in Liquid NO_2

This reaction was conducted by the procedure described above. Approximately 25 ml of liquid NO_2 was employed per 0.30 g of NO_2ClO_4.

3. Excess NO_2ClO_4 in Liquid SO_2

To a suspension of 0.340 g (2.32 mmoles) of NO_2ClO_4 in 25 ml of SO_2 was added 1.16 mmoles of NO. The temperature of the reaction mixture was maintained at -10°C for several hours. The volatile materials were removed by vacuum distillation.

4. Excess NO_2ClO_4 in CH_3NO_2

A solution of 0.490 g (3.38 mmoles) of NO_2ClO_4 in 20 ml of nitromethane was cooled to -196°C, and 1.69 mmoles of NO were added. After warming to room temperature, the solution was stirred for several hours. The product was isolated by distillation of the solvent in vacuo.

F. REACTION OF NO_2ClO_4 WITH NOF

A Kel-F reactor charged with 0.226 g (1.56 mmoles) of NO_2ClO_4 was attached to a metal vacuum line, and 2.0 mmoles of commercial NOF were condensed on the solid at -196°C. The reaction mixture was allowed to warm slowly to room temperature with stirring. The condensation process was repeated several times. The solid was isolated by removal of the volatile material in vacuo. A similar procedure was followed when NOF was generated in situ. The Kel-F reactor was charged with 0.876 g (6.04 mmoles) of NO_2ClO_4 and approximately 20 ml of liquid HF. Then 6.04 mmoles of NOCl was introduced at -196°C. The reaction mixture was kept at approximately -50°C for one hour and then allowed to warm slowly to room temperature. The white solid product was obtained by removal of the volatile materials in vacuo.

G. REACTION OF NO_2ClO_4 WITH CIS-N_2F_2

To 0.283 g (1.95 mmoles) of NO_2ClO_4 at -196°C was added 2.5 mmoles of cis-N_2F_2. The reaction mixture was allowed to warm to room temperature with stirring. The gas was recondensed on the NO_2ClO_4 several times. The N_2F_2 was recovered and identified by its infrared spectrum. The solid had an x-ray powder pattern consistent with that for NO_2ClO_4.

H. REACTION OF $N_2O_3(ClO_4)_2$ WITH NO_2BF_4

An acetonitrile solution of 0.425 g (3.2 mmoles) of NO_2BF_4 was added to a solution of 0.417 g (1.6 mmoles) $N_2O_3(ClO_4)_2$ in acetonitrile. Considerable gassing occurred, but no precipitation was observed. While the solvent was being distilled in vacuo, a leak developed in the system and the pasty mass obtained was discarded.

I. REACTION OF NO_2ClO_4 WITH SULFOLANE

When 7 ml of Sulfolane was added to 0.330 g of NO_2ClO_4, a red solution resulted. After stirring for 1/2 hour, 10 ml of $CHCl_3$ was added to this solution but no precipitation occurred. The solution was hydrolyzed, and the hydrolysate gave a positive test for ClO_4^- with ϕ_4AsCl reagent and a negative brown ring test for NO_3^-. In a second experiment, 2.93 mmoles of Sulfolane were added to a suspension of 0.426 g (2.93 mmoles) of NO_2ClO_4 in 7 ml of $CHCl_3$. The undissolved solid was isolated by filtration. Analysis is pending. The filtrate was hydrolyzed, and the hydrolysate gave a positive test for ClO_4^- and a negative brown ring test for NO_3^-.

IV. FUTURE WORK

- The products from the reactions of NO_2ClO_4 with NO, NOCl and NOF will be full characterized.

- The reaction of NO_2ClO_4 with Sulfolane will be investigated.

- Systems for the reaction of NO_2ClO_4 with fuel ligands such as NH_3 and N_2H_4 will be investigated.

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V. REFERENCES

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2. Report RMD 5017-Q1, Stabilization of High Energy Solid Oxidizer, Thiokol Chemical Corporation, Reaction Motors Division, 30 November 1962. (Contract NOnr 3913(00))

3. R. W. Sprague, Reactions of Oxides of Nitrogen with the Boron Halides, University Microfilms, Ann Arbor, Mich., L.C. Card No. Mic. 58-570, 1957.

Section IV

RMD Project 5009

INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

Section IV

INORGANIC CHEMISTRY OF THE OXYGEN SUBFLUORIDES

A. R. Young
S. I. Morrow
T. Hirata

Report RMD-AOR-Q1-63

FOREWORD

This report summarizes the results of studies of the reactions of
dioxygen difluoride conducted during the period 16 January 1963 to 1 April
1963 under Navy Contract NOnr 3824(00), ARPA Order No. 314-62. The
report has been published as Section IV of Report RMD-AOR-Q1-63. In
addition, it has been published separately as an unclassified document.

Personnel contributing to the work discussed in this section are as
follows: A. R. Young, II (Project Supervisor), T. Hirata, S. I. Morrow,
R. Storey, D. Y. Yee, and E. Egbert.

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ABSTRACT

Further characterization studies of the O_2F_2-Group V pentafluoride products were carried out during this quarter. Although the qualitative evidence that these products are dioxygenyl compounds of the form, O_2MF_6, remains convincing, quantitative analytical results presently available are still not completely satisfactory. Samples of the O_2F_2-AsF_5 product give consistently low arsenic analysis which is believed to be due to HF contamination. The best results have been obtained on the O_2F_2-SbF_5 product for which values of 46.07% and 46.05% have been obtained for Sb content, and 39.22% for fluorine content (theory for O_2SbF_6:Sb, 45.47; F, 42.59%).

I. INTRODUCTION

The overall objective of this research program is to generate basic information about the inorganic chemistry of the oxygen subfluorides (O_2F_2, O_3F_2, O_4F_2). It is hoped that this information may suggest routes to new inorganic solid oxidizers. Two general reactions of dioxygen difluoride which yield solid products are of current interest, namely, (a) the reaction of dioxygen difluoride with elemental chlorine or compounds containing monovalent chlorine, and (b) the reaction of dioxygen difluoride with pentafluorides of Group V elements. The former reaction yields violet-colored solids which are unstable above -80°C and must be characterized by examination of their decomposition products. The reaction of O_2F_2 with Group V pentafluorides produces solids which may be studied at room temperature. The work performed during this report period was primarily directed toward the characterization of the solid products obtained from O_2F_2-Group V pentafluoride reactions.

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II. DISCUSSION

The reactions of O_2F_2 with the pentafluorides of phosphorous, arsenic, and antimony have been previously reported (Ref 1 and 2). These reactions yield solid products having an order of stability which increases as the atomic weight of the Group V element increases. The least stable product, that obtained with phosphorous pentafluoride, decomposes rapidly in vacuo at ambient temperatures. The AsF_5 and SbF_5 products, on the other hand, require elevated temperatures ($>100°C$) for rapid decomposition. It is currently believed that these solid products are derivatives of the dioxygenyl cation, O_2^+ (Ref 3), which arise by the general reaction shown in equation 1.

$$O_2F_2 + MF_5 \xrightarrow{\ -160°C\ } O_2MF_6 + 1/2\ F_2 \tag{1}$$
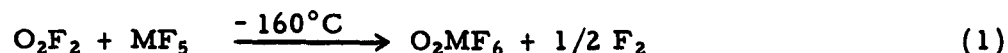
The evidence supporting this characterization may be summarized as follows:

- The noncondensable gases collected after completion of the reaction contain an excess of F_2 over O_2. (The presence of O_2 and F_2 in equimolar amounts is expected due to the decomposition of excess O_2F_2.)

- Oxygen can be detected by mass spectroscopy in the vapor phase above the solids at room temperature. At elevated temperatures, peaks are observed for the corresponding Group V pentafluoride.

- The infrared spectra of the O_2F_2-AsF_5 and O_2F_2-SbF_5 products show absorptions at 705 cm^{-1} for AsF_6^- and 669 cm^{-1} for SbF_6^-, respectively.

- The unstable O_2F_2-PF_5 product is converted to NO_2PF_6 by treatment with NO_2, and oxygen is liberated during the process.

- The x-ray diffraction pattern of the O_2F_2-AsF_5 product is almost identical to that of $NOAsF_6$.

- The O_2F_2-AsF_5 and O_2F_2-SbF_5 products liberate a mixture of O_2 and O_3 when treated with water.

In spite of these encouraging qualitative observations, attempts to obtain satisfactory analytical data in support of the characterization of these compounds as dioxygenyl derivatives have not been completely successful to date. Three methods of analysis have been used, namely, reaction with water (equation 2), reaction with NO_2 (equation 3) and thermal decomposition (equation 4).

$$2O_2MF_6 + H_2O \xrightarrow{\quad ? \quad} O_2 + O_3 + 2HMF_6 \tag{2}$$

$$NO_2 + O_2MF_6 \xrightarrow{\quad ? \quad} O_2 + NO_2MF_6 \tag{3}$$

$$O_2MF_6 \xrightarrow{\quad ? \quad} O_2 + 1/2F_2 + MF_5 \tag{4}$$
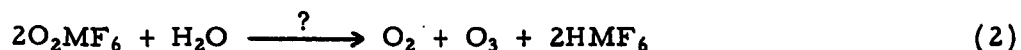
The results obtained in attempts to use hydrolysis and the reaction with nitrogen dioxide as analytical methods indicate that equation 2 and equation 3 are at least qualitatively correct, that is, oxygen and ozone are liberated when the O_2F_2-MF_5 products are treated with water and oxygen is liberated when the O_2F_2-MF_5 products are treated with NO_2. However, the quantities of gas liberated have been significantly lower than required by equations 2 and 3. Attempts to use thermal decomposition as an analytical method have been frustrated by the occurrence of side reactions between the initial decomposition products and the glass apparatus.

A. HYDROLYSIS OF DIOXYGENYL COMPOUNDS

Hydrolytic analysis was carried out on samples of the O_2F_2-AsF_5 products from two distinct preparative runs. If the O_2AsF_6 contents of the samples are calculated on the basis of the total oxygen and ozone found as compared to the amount predicted by equation 2 (Table I), one obtains values of 61.6% and 47.9%, respectively. On the other hand, the purities of the samples on the basis of their AsF_6^- contents shown in Table II (obtained by precipitating $\emptyset_4As(AsF_6)$ from the hydrolysate with $\emptyset_4AsCl$) are 90.5% and 86.7%, respectively. A possible reason for this discrepancy is that equation 2 does not accurately describe the reaction of O_2AsF_6 with water. An alternate equation which requires the liberation of less than a mole of gas per mole of O_2AsF_6 is shown in equation 5. Tests will be made for the presence of H_2O_2 in the hydrolysate.

$$O_2AsF_6 + 3/2 H_2O \longrightarrow HAsF_6 + H_2O_2 + 1/2 O_3 \tag{5}$$

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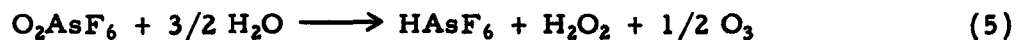
TABLE I

HYDROLYTIC ANALYSIS OF O_2F_2-AsF_5 PRODUCT

Sample Weight (gm)	O_2+O_3 Found (Total mmoles)	O_2+O_3 (calcd. by eq. 2) (Total mmoles)	AsF_6^- Found (%)	AsF_6^- (calcd. for O_2AsF_6) (%)
0.1728	0.48	0.78	77.41	85.51
0.1608	0.35	0.73	74.32	85.51

The low values obtained for the AsF_6^- content of the O_2F_2-AsF_5 product cannot be satisfactorily accounted for at this point. Emission spectra obtained on the samples show no lines other than those due to arsenic. The most reasonable explanation at present is that the samples contain HF. This will have to be confirmed by thermal decomposition studies in a Teflon or metal apparatus.

The analytical results obtained on the hydrolysates of the O_2F_2-SbF_5 product have been in much better agreement with theory than those obtained for the O_2F_2-AsF_5 product (Table II). However, as in the case of the arsenic product, the total gas $(O_2 + O_3)$ measured after hydrolysis of a sample of O_2SbF_6 is much lower than predicted by equation 2.

TABLE II

ANALYSIS OF O_2F_2-SbF_6 PRODUCT

Atom	Calcd. for O_2SbF_6 (%)	Found (%)
Sb	45.47	46.07, 46.05
F	42.59	39.22

B. REACTION OF DIOXYGENYL COMPOUNDS WITH NO_2

The reaction of NO_2 with O_2MF_6 compounds (equation 3) has been carried out by introducing NO_2 into the reactor immediately after separation of all

volatile by-products from the dioxygenyl compounds by pumping at -80°C.
The reaction has also been carried out on samples of the dioxygenyl compounds
which have been removed from the reactor in a dry atmosphere and weighed.
By both techniques, the oxygen found has been lower than predicted by equation
3, although in the former case this can be partially attributed to incomplete
conversion of the MF_5 compound to O_2MF_6.

The solid product obtained by the reaction of 1.14 mmoles AsF_5 with excess
O_2F_2, after pumping to remove all volatile by-products (O_2, F_2, SiF_4, unreacted
AsF_5), yielded 0.781 mmole oxygen upon reaction with excess NO_2 at room
temperature. Assuming complete conversion of the initial AsF_5 to O_2AsF_6, the
observed oxygen is only 70% of that required by equation 3. In a separate
experiment, a 0.140 g sample of the solid O_2F_2-AsF_5 product was allowed to
react with excess NO_2. The reaction evolved 0.0174 g O_2 giving an oxygen
content of 12.4% (required for O_2AsF_6, 14.5%).

Similar results were obtained with a freshly prepared sample of the
O_2F_2-PF_5 product. In another experiment, 1.31 mmoles of PF_5 were allowed
to react with excess O_2F_2, and materials volatile at -80°C (O_2, F_2, SiF_4,
POF_3, PF_5) were removed from the reactor. Treatment of the remaining
solid with excess NO_2 at 0°C produced 1.05 mmoles O_2. The residual solid
was identified as NO_2PF_6 by infrared spectroscopy.

C. THERMAL DECOMPOSITION OF DIOXYGENYL COMPOUNDS

The thermal decomposition of dioxygenyl compounds, O_2MF_6, should
proceed as shown in equation 4. The only test of this reaction as an analytical
method was carried out in a glass system with the O_2F_2-PF_5 product. A sample
of freshly prepared solid, which had been pumped at -80°C until it exhibited no
vapor pressure, was allowed to decompose at room temperature for two hours.
It formed 1.77 mmoles of gas of which 0.845 mmole was condensable at -196°C.
The fraction noncondensable at -196°C (0.925 mmole) did not decrease when it
was put in contact with mercury. It was identified as pure oxygen by mass
spectroscopy. The condensable fraction, which according to equation 4 should
have been PF_5, contained POF_3 and SiF_4, as well as PF_5. It is evident that
reactions with glass (equations 6 and 7) obscured the results obtained in this
analysis; therefore, they cannot be used to establish the composition of the
O_2F_2-PF_5 product.

$$2F_2 + SiO_2 \longrightarrow SiF_4 + O_2 \tag{6}$$

$$2PF_5 + SiO_2 \longrightarrow SiF_4 + 2POF_3 \tag{7}$$

— 6 —
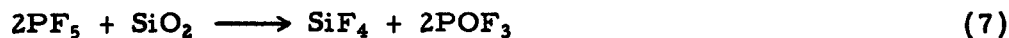
Future attempts to establish the composition of O_2F_2-MF_5 products by thermal decomposition will be carried out in Teflon or in metal systems.

D. INFRARED SPECTRA OF DIOXYGENYL COMPOUNDS

The infrared spectrum of the O_2F_2-AsF_5 product as a sodium fluoride pellet has been reported previously (Ref 2). An infrared spectrum of the O_2F_2-SbF_5 product appears in Figure 1. It shows a strong absorption at 669 cm^{-1} which has been reported for the SbF_6^- anion (Ref 4).

Because of the instability of the O_2F_2-PF_5 product, no attempt was made to obtain its infrared spectrum. When the unstable O_2F_2-PF_5 product is allowed to react with NO_2, it is converted to a thermally stable solid, the spectrum of which (Figure 2) shows absorptions for the NO_2^+ ion at 2350 cm^{-1} and for the PF_6^- anion at 837 cm^{-1} (Ref 4).

E. X-RAY DIFFRACTION PATTERNS OF DIOXYGENYL COMPOUNDS

The x-ray diffraction pattern of a new sample of the O_2F_2-AsF_5 product was obtained during this report period, and it is substantially identical to that previously reported (Ref 2). A powder sample of $NOAsF_5$ purchased from the Ozark-Mahoning Company was photographed for comparison with the arsenic compound. Its diffraction pattern (Table III) is almost identical to that of the O_2F_2-AsF_5 product.

Effort to confirm the powder diffraction pattern reported for the O_2F_2-SbF_5 product was unsuccessful (Ref 2). No diffraction pattern was obtained on the sample which gave the infrared spectrum shown in Figure 1. The reason for the failure to obtain a diffraction pattern for the O_2F_2-SbF_5 product has not as yet been determined.

F. REACTION OF O_2SbF_6 WITH HF

It is believed that NO_2SbF_6 is a minor impurity in the O_2F_2-SbF_5 product, since traces of brown vapors are evolved when it is hydrolyzed. The nitrogen evidently arises from air leaks in the system during the discharge preparation of O_2F_2 or is an impurity in the oxygen used in this preparation.

One approach to the purification of O_2SbF_6 is by recrystallization from a solvent. Hydrogen fluoride was, therefore, tested as a possible recrystalliza- tion medium. The condensation of HF onto a sample of the O_2F_2-SbF_5 product

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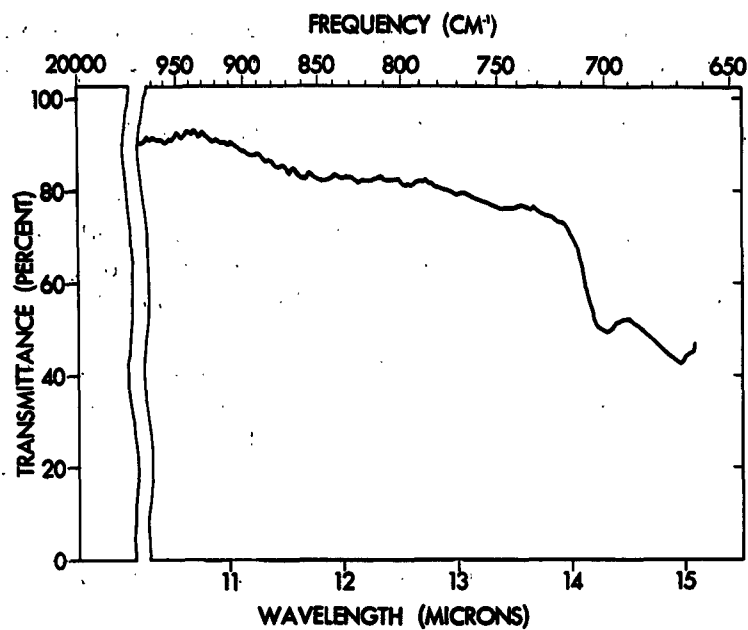
Figure 1. Infrared Spectrum of O_2SbF_6
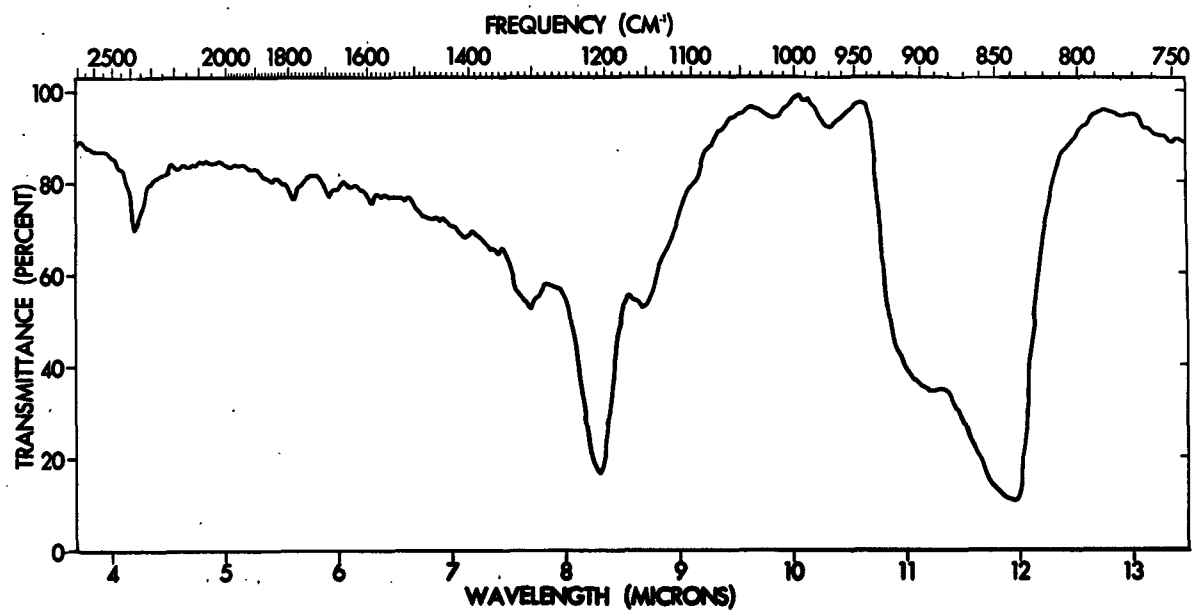
Figure 2. Infrared Spectrum of the NO_2-O_2PF_6 Product

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TABLE III

POWDER DIFFRACTION PATTERNS OF O_2F_2-AsF_5 PRODUCT AND NOAsF$_6$

Face Centered Cubic $a_0 = 8.00$ Å		O_2F_2-AsF_5 Product		NOAsF$_6$	
h, k, l	d, Å (calcd)	d, Å	I/I_0	d, Å	I/I_0
111	4.60	4.59	100	4.61	100
200	4.00	3.99	100	4.00	100
220	2.83	2.83	50	2.84	40
311	2.40	2.42	5	2.43	5
222	2.30	2.32	20	2.32	20
---	---	2.19	2	---	---
---	---	2.10	2	---	---
400	1.99	2.01	5	2.01	5
---	---	1.95	2	---	---
---	---	1.89	2	---	---
331	1.83	1.85	10	1.85	10
420	1.78	1.80	30	1.80	20
422	1.63	1.64	30	1.65	20
333, 511	1.54	1.55	20	1.55	15
---	---	1.49	2	---	---
---	---	1.44	4	---	---
440	1.41	1.42	4	1.42	2
531	1.36	1.36	10	1.36	5
442, 600	1.33	1.34	10	1.34	5
620	1.26	1.27	5	1.28	2
533	1.22	1.23	5	1.25	2
622	1.20	1.20	5	1.24	2

in a Kel-F tube gave rise to some interesting phenomena. A portion of the solid seemed to go into solution, and the surface of the undissolved solid appeared pink in the presence of HF. However, the color did not diffuse throughout the solution. The solvent and volatile reaction products were then condensed into a second Kel-F trap. It was evident that a highly corrosive, volatile material had been formed during treatment of the solid with HF, because the walls of the second trap became discolored when it warmed to room temperature. In spite of this evidence of reaction with HF, the solid remaining in the initial trap gave an infrared spectrum identical to the original O_2F_2-SbF_5 product (Figure 1). The study of the behavior of dioxygenyl compounds in HF will be pursued further in order to determine the extent of solubility and the nature of the observed interaction of the SbF_5 product with HF.

G. PREPARATION OF NEW DIOXYGENYL DERIVATIVES

1. Reaction of O_2 with ClO_3F

An attempt to prepare a dioxygenyl derivative having the ClO_3F^- anion by activating a mixture of oxygen and perchloryl fluoride in an electric discharge at -80°C was unsuccessful; both reagents were recovered.

2. Reaction of O_2F_2 with $SnCl_4$

Since most of the reactions of O_2F_2 studied on this program are carried out in glass apparatus, SiF_4 is an ever-present contaminant. It is surprising, therefore, that silicon does not appear as an impurity in the dioxygenyl compounds (as indicated by emission spectroscopy) in the form of $(O_2)_2SiF_6$. One possible explanation is that dioxygenyl compounds of bivalent complex fluoride anions are inherently unstable. This possibility was tested by attempting the preparation of $(O_2)_2SnF_6$ via the reaction shown in equation 8.

$$O_2F_2 \text{ (excess)} + SnCl_4 \xrightarrow{\ ?\ } (O_2)_2SnF_6 + 2Cl_2 \qquad (8)$$
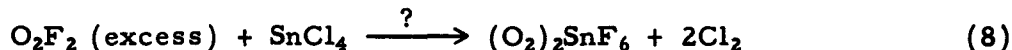
A reaction took place at the melting point of O_2F_2 giving rise to a violet-colored intermediate product, a behavior which is characteristic of O_2F_2 reactions with chlorine-containing reagents. The violet product decomposed on warming to room temperature, and chlorine was found to be the major component of the volatile decomposition products. A white solid remained at room temperature. Attempts to identify the solid by infrared, mass spectroscopy (elevated temperatures), and x-ray were unsuccessful, because the solid became contaminated

with water during handling. This reaction will be studied further in order to determine whether the solid is related to the products obtained by the reactions of Group V pentafluorides with O_2F_2.

3. Reaction of O_2F_2 with Xenon

Because of the current interest in compounds of the rare gasses, it was decided to attempt the preparation of dioxygenyl derivates of XeF_4 or XeF_6, as shown in equation 9.

$$O_2F_2 \text{ (excess)} + Xe \longrightarrow (O_2)_m XeF_n \qquad (9)$$
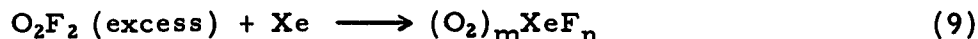
The reaction was initially carried out in a glass system by condensing Xe in the bottom of a glass U-shaped discharge tube, generating O_2F_2 in the apparatus at $-196°C$, and allowing the O_2F_2 to melt and flow on the solid Xe. The system was pumped at $-80°C$ until no vapor pressure remained at that temperature. Upon removal of the $-80°C$ bath, a solid was observed which built up a decomposition pressure as it warmed to room temperature. The solid appeared to decompose rapidly at room temperature. The resultant gases contained O_2, Xe, and SiF_4. Since it was suspected that the compound was reacting with the glass rather than decomposing thermally, the reaction was repeated in a Kel-F system. The solid appeared to disappear as rapidly at room temperature in Kel-F as it did in glass. During an attempt to remove a sample of the solid for mass spectral analysis, it was inadvertently exposed to air whereupon it fumed copiously. The mass spectrum of the vapors from this exposed sample showed Xe, H_2O, and HF.

Further studies of this reaction are in progress and it is hoped that additional evidence of the composition of this solid will be forthcoming.

H. Cl_2-O_2F_2 REACTION

No progress was made during this quarter in our continuing effort to characterize the unstable violet Cl_2-O_2F_2 addition product. Some studies were made of the "cold mercury absorption method" vs the "hot sodium chloride method" for analyzing oxygen-fluorine mixtures. On the basis of the results obtained, future analysis of the Cl_2-O_2F_2 decomposition products will be carried out by the cold mercury absorption method. The hot sodium chloride method invariably gave low results for fluorine due to a reaction with the glass apparatus producing SiF_4 and O_2.

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III. EXPERIMENTAL

A. O_2F_2-AsF_5 PRODUCT

The O_2F_2-AsF_5 reactions were carried out by condensing AsF_5 on the bottom of a U-shaped glass trap having copper electrodes sealed into each leg. A 1:1 mixture of O_2 and F_2 of sufficient quantity to produce a two-fold excess of O_2F_2 was leaked into the discharge tube (at $-196°C$) at a pressure of 10-15 mm, and discharge was maintained until the pressure decreased to zero. The Dewar was then lowered until the liquid nitrogen made contact only with the bottom of the U-trap. The O_2F_2 melted and flowed to the bottom where it reacted with the solid AsF_5. After the orange color of the O_2F_2 had been completely discharged, the liquid nitrogen Dewar was raised in order to condense unreacted AsF_5 and SiF_4, and a measured aliquot of the gas which was not condensable at $-196°C$ was taken in a mercury absorption tube of known volume. The liquid nitrogen bath was replaced by a Dry Ice-Trichlor bath ($-78°C$), and the system was evacuated until it exhibited no vapor pressure at $-78°C$.

1. Reaction of NO_2 with O_2F_2-AsF_5

A 1.14 mmole sample of AsF_5 was reacted with excess O_2F_2 as described above. The solid product (which exhibited no vapor pressure at $-78°C$) was treated with excess NO_2 at room temperature for 12 hours. After this period, the system was cooled to $-196°C$ and 0.781 mmole noncondensable gas was measured and identified as O_2 by mass spectroscopy. Based on equation 3 (i.e., $NO_2 + O_2AsF_6 \rightarrow O_2 + NO_2AsF_6$) the yield of O_2AsF_6 in the experiment was 68%.

In a similar experiment, the trap containing a freshly prepared sample of the O_2F_2-AsF_5 product was removed to a dry box, and a 0.140 g sample was placed in a glass bulb and allowed to react with excess NO_2. The sample liberated 0.0174 g O_2, which gives an O_2 content of 12.4% in the original sample (calculated for O_2AsF_6, 14.5%).

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2. Reaction of O_2F_2-AsF_5 Product with Water

Two hydrolysis experiments were carried out with weighed samples of the O_2F_2-AsF_5 product from different preparative runs. In the first, a 0.1728 g sample liberated 0.48 mmole of gas identified as a mixture of oxygen and ozone. The aqueous solution gave 0.4052 g of $\emptyset_4As(AsF_6)$ when treated with $\emptyset_4AsCl$. The AsF_6^- content was, therefore, 77.41% (calculated for O_2AsF_6, 85.51%). The sample from the second preparative run weighing 0.1608 g, liberated 0.35 mmole O_2 and O_3 (total) and yielded 0.3620 g $\emptyset_4AsAsF_6$. Its AsF_6^- content was, therefore, 74.32%.

B. O_2F_2-PF_5 PRODUCT

The O_2F_2-PF_5 reactions were carried out in a glass system using a procedure identical to that used for the O_2F_2-AsF_5 reaction.

1. Reaction of O_2F_2-PF_5 Product with NO_2

A 1.31 mmole sample of PF_5 was allowed to react with excess O_2F_2 at -160°C. After completion of the reaction, 0.71 mmole of condensable gas was removed from the reactor at -78°C and condensed at -196°C in a downstream trap. It contained SiF_4, POF_3, and a minor amount of PF_5. NO_2 was introduced into the reactor and allowed to remain in contact with the solid product at 0°C for two hours. At the end of this period, 1.05 mmoles of oxygen were measured in the system and identified by mass spectroscopy. Based on equation 3 (i.e., $NO_2 + O_2PF_6 \longrightarrow O_2 + NO_2PF_6$) the yield of O_2PF_6 in the reaction was 80%. The solid remaining after reaction with NO_2 showed an absorption at 2350 cm^{-1} for the NO_2^+ ion and at 837 cm^{-1} for the PF_6^- ion.

2. Thermal Decomposition of O_2F_2-PF_5 Product in Glass

The solid product obtained by the reaction of O_2F_2 with 1.31 mmoles PF_5 was allowed to decompose for 48 hours in a glass system of known volume. It liberated 1.77 mmoles of gas (calculated for 1.31 mmoles $O_2PF_6 \longrightarrow O_2 + 1/2 F_2 + PF_5$, 1.96 mmoles). The gas contained a 0.845 mmole fraction condensable at -196°C (POF_3, SiF_4, and PF_5) the balance (0.925 mmole) was virtually pure O_2.

C. O_2F_2-SbF_5 PRODUCT

1. Preparation of O_2F_2-SbF_5 Product in Kel-F Apparatus

Liquid SbF_5 was charged into a weighed Kel-F tube in a dry box. The tube was stoppered and reweighed (3.394 g SbF_5). The Kel-F tube was attached to the O_2F_2 generation system, while a positive pressure of dry N_2 was kept on the system to avoid diffusion of moist air into the SbF_5. O_2F_2 was prepared in a Kel-F discharge tube and distilled in vacuo onto the SbF_5 at $-196°C$. When the $-196°C$ bath was replaced with one at $-78°C$, the contents of the reactor appeared as an orange colored liquid. When this system was allowed to stand at $-78°C$ overnight, a light colored solid slowly formed. The product was pumped for several hours at room temperature to remove all volatile materials, including any SbF_5 which might not have reacted. The resulting gray-white solid weighed 3.569 g. This corresponds to an 85.3% yield of O_2SbF_6. Two attempts were made to obtain x-ray diffraction patterns of this material, but neither was successful. Hydrolysis of the product and chemical analysis of the resultant solution showed 46.05% Sb (45.47% theoretical). The infrared spectrum of the product showed an absorption at 669 cm^{-1} which is typical of SbF_6^-. When the product was allowed to react with NO_2 in a vacuum apparatus, a yellow solid was formed that released NO_2 on hydrolysis.

2. Reaction of O_2SbF_6 with HF

Anhydrous HF was condensed in a Kel-F tube containing a 1.04 g sample of O_2SbF_6. The solid had a faint pinkish-lavender color in the liquid HF at $-78°C$. It was difficult to determine whether the solution itself had a similar faint color or not. The solution was held overnight at $-78°C$. Although results of instrumental analysis of the gases from the reaction showed only air and oxides of nitrogen, there was some evidence (blackening of a Kel-F trap) that there may have been a reactive gas present. As the system was allowed to warm to room temperature, there appeared to be gassing at the surface of the solid, and the quantity of solid decreased appreciably. In order to determine whether a chemical reaction had taken place, the HF was pumped off and the solid residue analyzed. When the trap containing the solid product was removed from the system, the color changed from white to purple. This material proved to be more reactive on handling in the dry box under nitrogen than freshly prepared O_2SbF_6. However, its infrared spectrum was identical to those of samples of O_2SbF_6. The solid weighed 0.90 g after treatment with HF, a loss in weight of 0.14 g.

D. PREPARATION OF NEW DIOXYGENYL COMPOUNDS

1. Reaction of O_2 with ClO_3F

Equimolar quantities (approximately 1 mmole) of oxygen and perchloryl fluoride were charged into a 500 ml glass bulb. The mixture was allowed to leak into an evacuated quartz U-tube having sealed copper electrodes until the pressure in the discharge tube was 15 mm. The tube was cooled to -80°C, and a discharge was initiated by means of a 12,000 volt luminous tube transformer. No decrease in pressure was observed over a two-hour period and after the discharge was terminated, and no solid product was in the discharge tube.

2. Reaction of $SnCl_4$ with O_2F_2

After thorough degassing, approximately 5 ml (0.27 mmole) of $SnCl_4$ was condensed in an O_2F_2 generator. O_2F_2 was prepared in the arc and slowly brought into contact with the solid $SnCl_4$. An intense purple color appeared upon contact. On rapid warming of the mixture, there was a pressure surge resulting in information of noncondensable gases. The purple material rapidly decomposed at -78°C. A dark ring remained on the wall which turned purple upon recondensation of the gases present. On long standing, the dark material bleached white. Solid material was recovered at room temperature. Although mass spectral and infrared analyses were made, the presence of H_2O in the sample renders interpretation of the data impossible. X-ray analysis is being carried out on a sample of the solid. The condensable gas was primarily Cl_2. No Cl-O bonded materials were found.

3. Reaction of Xenon and O_2F_2

Gaseous xenon was condensed at -196°C in the bottom of a Kel-F electrical discharge tube, and O_2F_2 was then generated in the same trap. When the cold bath was lowered, there was no evidence of the orange-colored liquid, O_2F_2. Instead only a light yellow solid was seen. This solid was frozen at -196°C and outgassed to remove any free O_2 or F_2 present. Mass spectrometric analysis of the gases given off by the solid at room temperature indicated the presence of xenon. The sample was stored overnight at -78°C. The U-trap was inadvertently broken during an attempt to remove it from the vacuum system to a dry box. The grayish-white solid in the trap began to fume as it came in contact with moist air. Although it was placed in a dry box immediately, it appeared to be decomposing rapidly, giving off noxious fumes. In spite of

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these difficulties, a small sample of the solid was loaded into a metal tube for pyrolysis in a mass spectrometer. When the sample was heated, small amounts of xenon along with water and HF were evolved.

E. ANALYSIS OF OXYGEN-FLUORINE MIXTURES

1. Analysis of a Sample of O_2 and F_2 by Sodium Chloride Method

Approximately 0.5 mmole of a 1:1 mixture of O_2 and F_2 was slowly passed through NaCl previously heated to 120°C. The Cl_2 resulting from the reaction of F_2 with NaCl was trapped at -196°C. The O_2 was transferred to a calibrated volume by means of a Toepler pump. The noncondensables amounted to 0.297 mmole, of which about 5% was a CF_4 impurity and the remainder was O_2. This was determined by mass spectroscopy. The condensable fraction was 0.161 mmole of Cl_2 with a trace of SiF_4. These data give an O_2/F_2 ratio of 1.8.

2. Analysis of O_2 and F_2 by Mercury Absorption

A 1:1 mixture of O_2 and F_2 was expanded into a glass cylinder having stop-cocks at each end. One end was attached to the vacuum manifold by means of a ball joint and the other end to a mercury reservoir. The aliquot was 0.336 mmole. A small amount of mercury was admitted and the container was shaken for several hours. The surface of the mercury became tarnished by reaction with fluorine. The unreacted O_2 was transferred to a calibrated volume and measured. Mass spectral analysis indicated traces of SiF_4 and CF material. The O_2 amounted to 0.159 mmole. This gives an F_2/O_2 ratio of 1.17, or approximately 1:1.

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IV. FUTURE WORK

- The analysis of the O_2F_2-Group V pentafluoride reaction product will be continued.

- The physical and chemical properties of the O_2F_2-Group V pentafluoride products will be investigated.

- The reactions of O_2F_2 with $SnCl_4$ and with xenon will be studied further.

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V. REFERENCES

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